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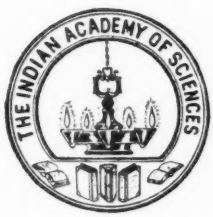

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HETEROCYCLIC COMPOUNDS.

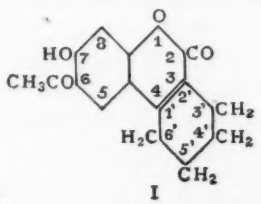
Part VII. Coumarins from Resacetophenone and Cyclic-β-ketonic Esters.

By Nazir Ahmad Chowdhry
and
R. D. Desai.

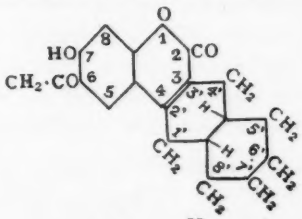
(*From the Department of Chemistry, Muslim University, Aligarh.*)

Received May 6, 1938.
Received in Revised form on June 6, 1938.
(Communicated by Dr. R. K. Asundi, M.Sc., Ph.D.)

Desai and Hamid[1] showed that resacetophenone condensed with aceto-acetic ester in the presence of phosphorus oxychloride with the formation of 7-hydroxy-6-acetyl-4-methylcoumarin. Extending this reaction to ethylcyclohexanone-2-carboxylate, we find that resacetophenone under similar conditions, gives 7-hydroxy-6-acetyl-(1' : 2' : 4 : 3)-cyclohexeno-coumarin (I). Its constitution was established by the fact that it gave a strong ferric chloride reaction showing the *ortho*-position of OH and $-COCH_3$ groups. Further, reduction by Clemmensen's method gave 7-hydroxy-6-ethyl-(1' : 2' : 4 : 3)-cyclohexeno-coumarin which was also prepared for comparison by condensing 4-ethyl-resorcinol with cyclohexanone-2-carboxylate in the presence of concentrated sulphuric acid.



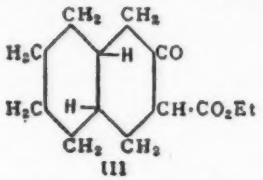
I



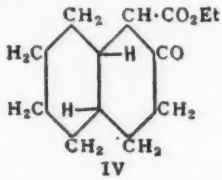
II

Other cyclic-β-ketonic esters like 4-methylcyclohexanone-2-carboxylate, 5-methylcyclohexanone-2-carboxylate and *trans*-β-decalone-3-carboxylate condensed similarly with resacetophenone with the formation of 7-hydroxy-6-acetyl-4'-methylcyclohexeno-(1' : 2' : 4 : 3) ; 7-hydroxy-6-acetyl-5'-methyl-cyclohexeno-(1' : 2' : 4 : 3)-, and 7-hydroxy-6-acetyl-*trans*-octalino-(2': 3': 4: 3)-coumarins (II). As each of them was reducible by zinc amalgam to their 7-hydroxy-6-ethyl analogues which could be easily prepared from 4-ethyl-resorcinol and the respective β-ketonic esters, the constitution of these coumarins was clearly established.

Ethyl-2-keto-*trans*-decalin-3-carboxylate was prepared by the application of Kötz's[2] method; according to Hückel and Goth,[3] but the latter investigators have not determined the constitution. We found that oxidation with alkaline potassium permanganate gave a quantitative yield of *trans*-cyclohexane-1 : 2-diacetic acid; which could arise only from 3-carboxylate (III) and not from 1-carboxylate (IV).



III



IV

6-Methylcyclohexanone-2-carboxylate did not react with resacetophenone in the presence of phosphorus oxychloride. We are busy condensing these esters with substituted resacetophenones as well as the preparation of coumarino-chromones from these coumarins.

Experimental.

7-Hydroxy-6-acetyl-cyclohexeno-(1' 2' : 4 : 3)*-coumarin.*—A mixture of cyclohexanone-2-carboxylate (5 g.), resacetophenone (4.5 g.), phosphorus oxychloride (3 c.c.) and dry benzene (25 c.c.) was heated on the water-bath under reflux for three hours. The benzene solution was poured off, and the sticky, black residue was thrice extracted with benzene (15 c.c., each lot). The residue left after the removal of benzene crystallised from dilute alcohol in needles, m.p. 237° C. (Found: C, 69·5; H, 5·5; $C_{15}H_{14}O_4$ requires C, 69·8; H, 5·4 per cent.) The coumarin is soluble in alcohol, acetone, benzene and glacial acetic acid but sparingly soluble in hexane and petrol. Its alcoholic solution gives a reddish-violet colouration with ferric chloride.

The *acetyl derivative* prepared by heating the coumarin (0·5 g.) with acetic anhydride (5 c.c.) on a sand-bath for three hours, crystallised from dilute alcohol in needles melting at 199° C. (Found: C, 67·9; H, 5·4; $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3 per cent.)

Reduction to 7-hydroxy-6-ethyl-cyclohexeno-(1' : 2' ; 4 : 3)*-coumarin.*—An alcoholic solution of the above coumarin (0·5 g.) was added to amalgamated zinc dust (5 g.) covered with hydrochloric acid (15 c.c.) and the mixture was heated under reflux on sand-bath for three hours. The precipitate obtained on cooling was filtered off, extracted with alcohol to get rid of zinc dust and the alcoholic solution concentrated, when prismatic needles melting at 218°C. were obtained. This was identical in m.p. and mixed m.p. with the

coumarin obtained from 4-ethylresorcinol and cyclohexanone-2-carboxylate, by Z. Ahmad and Desai.[4]

7-*Hydroxy*-6-*acetyl*-4'-*methylcyclohexano*-(1' : 2' : 4 : 3)-*coumarin*, was similarly prepared from resacetophenone (5 g.), 4-methylcyclohexanone-2-carboxylate (5 g.), $POCl_3$ (3 c.c.), and dry benzene (20 c.c.) as usual, and crystallised from dilute alcohol in fine needles melting at 262° C. Its alcoholic solution gave a reddish-brown colour with ferric chloride. (Found : C, 70·4 ; H, 5·8 ; $C_{16}H_{16}O_4$ requires, C, 70·6 ; H, 5·9 per cent.) Reduction with amalgamated zinc dust gave 7-*hydroxy*-6-*ethyl*-4'-*methylcyclohexeno*-(1' : 2' : 4 : 3)-*coumarin*, identified by m.p. and mixed m.p. with an authentic specimen.

A mixture of 4-ethylresorcinol (3 g.), 4-methylcyclohexanone-2-carboxylate (3 g.) and concentrated sulphuric acid (10 c.c.) was left overnight and poured over ice. The solid crystallised from dilute alcohol in tiny plates melting at 252° C. It dissolved in alkali with a yellow colour and blue fluorescence. (Found : C, 74·1 ; H, 7·1 ; $C_{16}H_{18}O_3$ requires C, 74·4 ; H, 7·0 per cent.) The *acetyl derivative* crystallised from dilute alcohol in lustrous plates melting at 146° C. (Found : C, 72·1 ; H, 6·8 ; $C_{18}H_{20}O_4$ requires C, 72·0 ; H, 6·7 per cent.) The *methyl ether* prepared by shaking the alkaline solution of the coumarin with dimethyl sulphate crystallised from dilute alcohol in flat needles melting at 158° C. (Found : C, 74·8 ; H, 7·6 ; $C_{17}H_{20}O_3$ requires C, 75·0 ; H, 7·6 per cent.)

7-*Hydroxy*-6-*acetyl*-5-*methylcyclohexeno*-(1' : 2' : 4 : 3)-*coumarin*, was prepared from resacetophenone (3 g.), 5-methylcyclohexanone-2-carboxylate (3 g.), $POCl_3$ (3 c.c.) and dry benzene (20 c.c.) by the usual method and crystallised from dilute alcohol in small needles melting at 258° C. Its alcoholic solution gave a reddish colour with ferric chloride. (Found : C, 70·6 ; H, 6·0 ; $C_{16}H_{16}O_4$ requires C, 70·6 ; H, 5·9 per cent.) It could be reduced to 7-*hydroxy*-6-*ethyl*-5'-*methylcyclohexeno*-(1' : 2' : 4 : 3)-*coumarin*, identified by m.p. and mixed m.p. with an authentic specimen.

7-*Hydroxy*-6-*ethyl*-5'-*methylcyclohexeno*-(1' : 2' : 4 : 3)-*coumarin*, was obtained by the usual method from 4-ethylresorcinol and 5-methylcyclohexanone-2-carboxylate and crystallised from dilute alcohol in small plates melting at 202° C. The yellowish alkaline solution gave blue fluorescence, while its solution in concentrated sulphuric acid gave violet fluorescence. (Found : C, 74·2 ; H, 6·9 ; $C_{16}H_{18}O_3$ requires C, 74·4 ; H, 7·0 per cent.) The *acetyl derivative* crystallised from dilute alcohol in fine needles melting at 167° C. (Found : C, 71·8 ; H, 6·9 ; $C_{18}H_{20}O_4$ requires C, 72·0 ; H, 6·7 per cent.). The *methyl ether* crystallised from alcohol in lustous plates

melting at 127° C. (Found : C, 74·9 ; H, 7·7 ; $C_{17}H_{20}O_3$ requires C, 75·0 ; H, 7·6 per cent.)

Preparation of trans-*β-decalone-3-carboxylate.*—This was prepared by a slight modification of the method of Hückel and Goth (*loc. cit*).

To a cooled solution of sodium ethoxide (6·6 g. Na ; 80 c.c. absolute alcohol) a mixture of *trans-β*-decalone (42 g.) and absolute ethyl oxalate (42 g.) was slowly added with constant shaking, and the mixture allowed to stand in ice-cold water for six hours and then at the ordinary temperature for four days. The mixture was freely diluted with water, and made slightly acidic with ice-cold hydrochloric acid, when a thick oil was precipitated. This was extracted with ether, and the ethereal solution was extracted with 5 per cent. NaOH solution to remove the unreacted decalone. The alkaline solution on acidification gave almost pure *trans-β*-decalone-3-glyoxalate which was extracted with ether, dried and recovered. Its alcoholic solution gave a blood-red coloration with ferric chloride. It was heated in an oil-bath at 180° C. for two hours, taken up in ether, and the ethereal solution extracted with 5 per cent. NaOH solution to remove *β*-decalone which was also formed as a by-product during heating. The alkaline solution on acidification, gave *trans-β*-decalone-3-carboxylate which was extracted with ether, dried and distilled. It boiled at 145–50° C./6 mm. and immediately solidified on cooling to large, beautiful, rectangular plates, melting at 46° C. It could be easily crystallised from hexane. Its alcoholic solution gave indigo-blue colour with ferric chloride.

Oxidation to trans-*cyclohexane*-1 : 2-*diacetic acid.*—To the ester (0·5 g.) dissolved in N/10 NaOH (20 c.c.) 5 per cent. potassium permanganate (40 c.c.) was gradually added, and thoroughly shaken. Sulphur dioxide was passed to remove the excess of permanganate and the precipitated manganese dioxide was filtered off. The alkaline solution was concentrated on the sand-bath, and strongly acidified with concentrated hydrochloric acid, when a crystalline acid melting at 164° C. was obtained. This was identified as *trans*-cyclohexane-1 : 2-diacetic acid by mixed melting point with an authentic specimen obtained by oxidising *trans-β*-decalone with concentrated nitric acid according to the instructions of Kandiah.[5]

7-*Hydroxy*-6-*acetyl*-trans-*octalino*-(2' : 3' : 4 : 3)-*coumarin*, was prepared by the usual method from resacetophenone (3 g.), *trans-β*-decalone-3-carboxylate (3 g.), $POCl_3$ (2 c.c.) and dry benzene (15 c.c.). The coumarin crystallised from dilute alcohol in fine needles melting at 250° C. Its alcoholic solution gave brownish-red coloration with ferric chloride. (Found : C, 73·0 ; H, 6·5 ; $C_{19}H_{20}O_4$ requires C, 73·1 ; H, 6·4 per cent.) When reduced

by amalgamated zinc, it gave 7-*hydroxy*-6-*ethyl*-trans-*octalino*-(2' : 3' : 4 : 3)-*coumarin*, which was also obtained by condensing 4-ethylresorcinol (3 g.) with *trans*-β-decalone-3-carboxylate (4·4 g.) in presence of concentrated sulphuric acid (15 c.c.). It crystallised from dilute alcohol in needles melting at 308° C. This coumarin forms a sparingly soluble sodium salt when treated with a dilute solution of caustic soda, and gives blue fluorescence. It could not be methylated by alkali and dimethyl sulphate. (Found : C, 76·2 ; H, 7·3 ; $C_{19}H_{22}O_3$ requires C, 76·5 ; H, 7·4 per cent.)

The *acetyl derivative* crystallised from dilute alcohol in needles melting at 172° C.(Found : C, 73·9 ; H, 7·2 ; $C_{21}H_{24}O_4$ requires C, 74·1 ; H, 7·0 per cent.)

Summary.

Resacetophenone has been condensed with cyclic-β-ketonic esters like cyclohexanone-2-carboxylate, alkylcyclohexanone-2-carboxylates and *trans*-β-decalone-3-carboxylate in the presence of phsophorus oxychloride with the formation of 7-hydroxy-6-acetyl derivatives of cylcohexeno- and octalino-coumarins.

REFERENCES.

1. Desai and Hamid, *Proc. Ind. Acad. Sci.*, 1937, **6**, 185.
2. Kötz, *Annalen*, 1925, **342**, 346.
3. Hückel and Goth, *Ber.*, 1925, **58**, 447.
4. Z. Ahmad and Desai, *Jour. Univ. Bombay*, 1937, **6**, (2), 89.
5. Kandiah, *J.*, 1931, 935.

DIFFRACTION OF LIGHT BY SUPERPOSED ULTRASONIC WAVES.

By M. A. Govinda Rau.

Received July 11, 1938.

In his recent book on *Der Ultraschall*, L. Bergmann has reproduced some striking pictures of the diffraction effects observed when a beam of light traverses normally an ultrasonic sound field produced by a quartz crystal immersed in a liquid and simultaneously excited at two of its harmonics. If $k_1 n$ and $k_2 n$ are the two harmonics, then beside the diffraction lines due to $k_1 n$ and $k_2 n$, combinational lines due to $k_1 n \pm k_2 n$ also appear. A reference to the original paper[1] (1934) showed that he had also obtained similar combinational lines with crystals of different thicknesses, simultaneously excited at two incommensurate frequencies. Early this year, in January, it was thought that a natural explanation for this phenomenon could be provided by the simple theory of Raman and Nath.[2] Actually Mr. Nagendra Nath in a private communication to Prof. Sir C. V. Raman, had indicated that according to the theory, the consequence of such a superposition of two wave systems would be to give rise to the appearance of new combinational lines, whose number and intensity will vary much with the intensity of either of the original lines. Thus new lines corresponding to $rn_1 \pm sn_2$ will occur, the intensity being given by the expression

$$J_r^2 (v_1)\, J_s^2 (v_2),$$

where $J_r (v_1)$ is a Bessel function of the rth order, and $v_1 = \frac{2\pi \mu_1 l}{\lambda}$, μ_1 being the maximum change in refractive index in the liquid, l the length of the light path in the sound field, and λ the wave-length of light.

In order to verify these conclusions, it was thought worthwhile to repeat Bergmann's experiments more systematically, and with different sets of frequencies and intensities. The work had been partly completed when another paper by L. Bergmann[3] (1938) appeared, in which besides some of our observations, further extensions of same to diffraction by sound waves set up in glass, have been beautifully recorded. However, we publish herewith some of our pictures, illustrating the effects of varying intensities clearly. In Fig. 1, two different intensities of the first order in (*a*) were obtained by slight obliquity of incidence, and similarly also for the

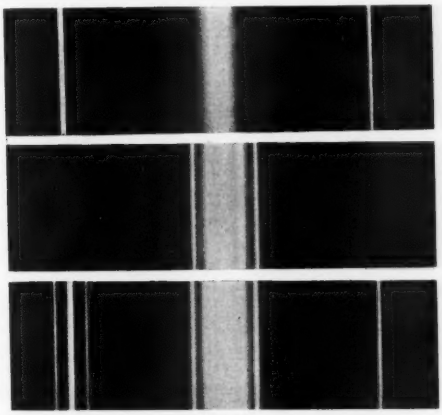


FIG. 1.

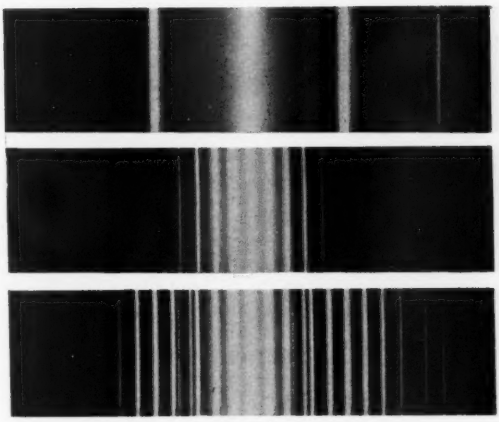


FIG. 2.

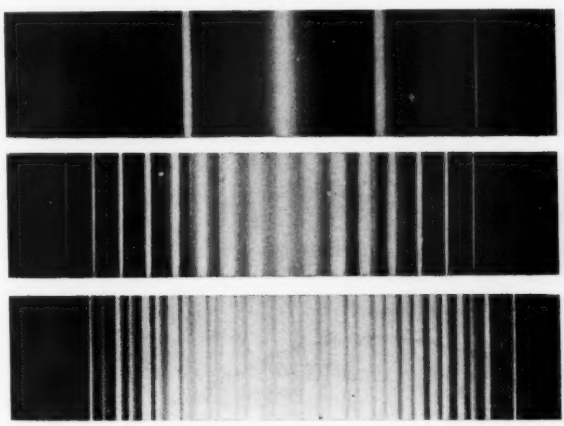


FIG. 3.

second orders in Fig. 2 (*a*). As is clear from the pictures in Fig. 1, the combination lines come out considerably brighter about the stronger first order on the left. Similarly in Fig. 2 (*c*), the larger number of combinational lines on the right are due to the additional lines arising out of the second order line. Fig. 3 is reproduced just to illustrate further the large number of combinational lines made visible, when one of the spectra (*b*) is strongly developed: combinations such as $n_2 \pm 8n_1$, $2n_2 \pm 5n_1$ can be identified in the picture.

The experiments were all carried out in the usual manner, but with two different crystals excited by separate oscillators, and immersed in xylol vertically at the opposite ends of a square glass trough.

Some theoretical aspects of these combination lines have also been worked out here by Mr. K. N. Rao, but they will not be reproduced here in view of the recent publications of the full papers by Nagendra Nath[4] and also by E. Feus.[3]

The author takes great pleasure in expressing in this connection his gratitude to Prof. Sir C. V. Raman, at whose suggestion this work was taken up before Bergmann's second paper appeared.

Summary.

Pictures are reproduced of the diffraction patterns obtained with light that has traversed a system of superposed ultrasonic waves set up in a liquid. Besides the presence of the combinational lines, the pictures clearly show the characteristic manner in which their number and intensities depend upon the intensity of the original spectral orders.

REFERENCES.

1. L. Bergmann .. .. .. *Z. Hochfrequenz Tech.*, 1934, **43**, 83.
2. C. V. Raman and N. S. N. Nath .. *Proc. Ind. Acad. Sci.*, (A), 1935, **2**, 406, 413.
3. L. Bergmann and E. Feus .. *Z. Physik*, 1938, **109**, 1.
4. N. S. N. Nath .. .. .. *Proc. Cambr. Phil. Soc.*, 1938, **34**, 213.

AN APPLICATION OF THE BI-PARTITIONAL FUNCTION Hg (P, Q) IN THE ENUMERATION OF DIFFERENT SAMPLES FROM FINITE POPULATION.

By P. V. Sukhatme, B.Sc., Ph.D.

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Received June 22, 1938.

(Communicated by Prof. P. C. Mahalanobis, I.E.S.)

The bi-partitional function Hg (P, Q) is defined as

$$h_{p_1}h_{p_2}\cdots h_{p_\rho} = \Sigma \text{Hg (P, Q)}\, g\,(q_1\, q_2\cdots q_\sigma) \qquad (1)$$

where P and Q stand for the partitions $(p_1\, p_2\cdots p_\rho)$ and $(q_1\, q_2\, \cdots q_\sigma)$ respectively of the same partible number $\omega\ (= \Sigma p_i = \Sigma q_i)$; $g\,(q_1\, q_2\cdots q_\sigma)$ is a monomial symmetric function of the quantities $x_1\, x_2\cdots$given by

$$g\,(q_1\, q_2\, \cdots q_\sigma) = \Sigma\,(x_1^{q_1}\ x_2^{q_2}\ \cdots\ x_\sigma^{q_\sigma}), \qquad (2)$$

the h-function of the pth degree called the homogeneous product sum is given by

$$h_p = \Sigma g\,(p) \qquad (3)$$

the summation being taken over all the monomial symmetric functions represented by the partitions of the number p ; and the summation Σ in equation (1) is taken over all partitions Q of the weight ω. The properties of this bi-partitional function, its connection with distributions *in plano* and with the combinatorial problem of which it affords solution and the arithmetical method of evaluating it for large partitions are described in detail in a recent paper by the author in the *Phil. Trans.*[1] The practical method of its evaluation put forth in the above paper is primarily due to R. A. Fisher. It is proposed in this note to exhibit its application in the enumeration of different samples of given size drawn from a finite population.

We shall do well to recall the arithmetical method of evaluating Hg (P, Q). We need consider the special case when either P or Q contains two parts only. Let $\text{P} = (p_1, p_2\cdots p_\rho)$ and $\text{Q} = (q, \omega - q)$. For evaluating Hg (P, Q), all the different partitions of q or $(\omega - q)$ whichever is less, having parts less than or equal to ρ are listed and the numbers of ways in which the parts of each of the different partitions of q or $(\omega - q)$ are obtained from the parts of P are recorded. The sum for all partitions represents Hg (P, Q). Thus to evaluate Hg $(42^2, 53)$: The different partitions of 3 having parts less than or equal to $\rho - 3$, are recorded. These are (3), (21) and (1^3). The

[1] P. V. Sukhatme, *Phil. Trans. Roy. Soc. London*, A, No. 780, Vol. **237**, 375-409.

part 3 of the partition (3) may be obtained from the parts of (42^2) in one way only ; the parts 2, and 1, may be obtained in six ways from the parts of (42^2) and finally the parts of (1^3) may be obtained in one way only from the parts of (42^2). The process is sy.tematical'y carried out as follows :

	(3)	(21)	(1^3)	
(42^2)	1	6	1	8

giving Hg (P, Q) = 8.

A partition $(p_1\, p_2 \cdots p_\rho)$ may be interpreted to mean that of the $\omega = \Sigma p_i$ quantities comprising a finite population p_1 quantities have a value 1 each ; p_2 have a value 2 each and so on. Conversely a finite population of size ω can always be specified by a partition of the same weight ω.

The total number of ways in which samples of size q can be drawn from a population of size ω is $\frac{\omega\,!}{q\,!\,(\omega - q)\,!}$, and is obviously equal to the number of ways of drawing samples of size $(\omega - q)$ from a population of the same size. All the $\frac{\omega\,!}{q\,!\,(\omega - q)\,!}$ samples will not however be different in composition giving different moment-statistics. The number of different samples of size q which can be drawn from the population $(p_1\, p_2 \cdots p_\rho)$, will necessarily be represented by such partitions of the number q, which have the number of parts less than or equal to ρ and whose parts are chosen in all different ways from the parts of the partition $(p_1,\ p_2 \cdots p_\rho)$. The arithmetical process described above clearly shows that the number of different samples of size q drawn from the population $(p_1\, p_2 \cdots p_\rho)$ of size ω is given by Hg (P, Q) ; where P $\equiv (p_1\, p_2 \cdots p_\rho)$ and Q $\equiv (q,\ \omega - q)$ or *vice versa* since Hg (P, Q) $\equiv$ Hg (Q, P).

To take an example, suppose we have a population represented by the partition (1, 6, 8 12,). The interpretation attached to this partition is that of the 27 quantities comprising this population, 1 has a value one, 6 have values two each, 12 have values three each and the remaining 8 have values 4 each. The population will be represented by means of a frequency distribution as follows :

Value of the variate	..	1	2	3	4
Frequency	..	1	6	12	8 = 27

The problem is to enumerate all the different samples of size, say 8, which can be drawn from this population. The necessary ca'cu'ations are shown below :—

Partitions of 8 of parts $\leqslant 4$	No. of different samples	Specification 1 2 3 4	Frequency
(8)	2	. . 8 .	495
		. . . 8	1
(71)	6	. . 1 7	96
		. 1 . 7	48
		1 . . 7	8
		. . 7 1	6336
		. 1 7 .	4752
		1 . 7 .	792
(62)	6	. 2 . 6	420
		. . 2 6	1848
		. 2 6 .	13860
		. . 6 2	25872
		. 6 2 .	66
		. 6 . 2	28
(53)	6	. 5 3 .	1320
		. 5 . 3	336
		. 3 5 .	15840
		. . 5 3	44352
		. 3 . 5	1120
		. . 3 5	12320
(4^2)	3	. 4 4 .	7425
		. . 4 4	34650
		. 4 . 4	1050
(61^2)	9	1 6 1 .	12
		1 6 . 1	8
		1 6 1 1	96
		1 1 6 .	5544
		1 . 6 1	7392
		. 1 6 1	44352
		1 1 . 6	168
		1 . 1 6	336
		. 1 1 6	2016
(521)	12	1 2 5 .	11880
		1 2 . 5	840
		1 . 2 5	3696
		1 5 2 .	396
		1 5 . 2	168
		1 . 5 2	22176
		. 1 5 2	133056
		. 1 2 5	22176
		. 2 5 1	95040

Partitions of 8 of parts $\leqslant 4$	No. of different samples	Specification 1 2 3 4	Frequency
		· 2 1 5	10080
		· 5 1 2	2016
		· 5 2 1	3168
(431)	12	1 4 3 ·	3300
		1 3 4 ·	9900
		1 · 4 3	27720
		1 · 3 4	15400
		1 4 · 3	840
		1 3 · 4	1400
		· 1 4 3	166320
		· 1 3 4	8400
		· 4 3 1	26400
		· 4 1 3	10080
		· 3 1 4	16800
		· 3 4 1	79200
(42^2)	3	· 4 2 2	27720
		· 2 4 2	207900
		· 2 2 4	69300
(3^22)	3	· 3 3 2	123200
		· 3 2 3	73920
		· 2 3 3	184800
(51^3)	3	1 5 1 1	576
		1 1 5 1	38016
		1 1 1 5	4032
(421^2)	6	1 4 2 1	7920
		1 4 1 2	5040
		1 2 4 1	59400
		1 2 1 4	12600
		1 1 4 2	83160
		1 1 2 4	27720
(32^21)	3	1 3 2 2	36960
		1 2 3 2	92400
		1 2 2 3	55440
(3^21^2)	3	1 3 3 1	35200
		1 3 1 3	13440
		1 1 3 3	73920
TOTAL ..	77		$\left(\frac{27\,!}{8\,!\,19\,!}\right)$

It will be seen that the number of different samples is 77 which is equal to Hg {(1, 6, 12, 8) ; (8, 19)} ≡ Hg {(8, 19,) ; (1, 6, 12, 8)}.

HETEROCYCLIC COMPOUNDS.

Part VIII. Coumarins from Alkylcyclohexanone-2-carboxylates and *Trans*-β-decalone-3-carboxylate.

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In continuation of our work on the synthesis of coumarins from cyclic-β-ketonic esters,[1] we have now extended this investigation to the preparation of coumarins from 4-methyl-, 5-methyl-, and 6-methyl-cyclohexanone-2-carboxylates as well as *trans*-β-decalone-3-carboxylate by the Pechmann method. 5-Methylcyclohexanone 2-carboxylate has already been condensed with phloroglucinol, orcinol and pyrogallol in the presence of concentrated sulphuric acid, by Sen and Basu,[2] but we find that improved yields of the coumarins from these phenols are obtained by using phosphorus oxychloride, while concentrated sulphuric acid is the best condensing agent for resorcinol and α-naphthol.

Exactly identical results were obtained with 4-methyl-cyclohexanone-2-carboxylate and *trans*-β-decalone-3-carboxylate which condensed readily with the above phenols, but 6-methylcyclohexanone-2-carboxylate underwent coumarin condensation with all these phenols only in the presence of phosphorus oxychloride.

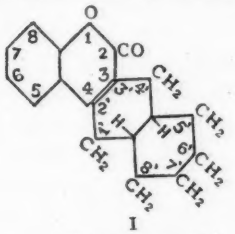
We have assumed the coumarin structure for all these products because of their unusual stability to the action of hot concentrated alkali. Sen and Basu (*loc. cit.*) have also observed the same stability in the case of their coumarins. If they had the alternative structure of substituted tetrahydroxanthones or cyclohexenochromones, they would have readily undergone fission to the alkylcyclohexanones and resorcylic acid as observed by Desai and Zafar-Uddin[3] in the case of cyclopentenochromones.

Sen and Basu (*loc. cit*) assumed that the coumarin obtained from orcinol and 5-methylcyclohexanone-2-carboxylate had the structure of 7-hydroxy-5-methyl-5′-methyl cyclohexeno-(1′ : 2′ : 4 : 3) coumarin but the absence of fluorescence and yellow colour of the alkali solution of these coumarins are against the 7-hydroxy structure. Therefore, we believe that this coumarin is 5-hydroxy-7-methyl-5′-methylcyclohexeno-(1′ : 2′ : 4 : 3)-coumarin, and the

same is the case with the other coumarins from orcinol. We have subjected the acetates of the coumarins from resorcinol and cyclic-β-ketonic esters to the Fries' Transformation in the presence of anhydrous aluminium chloride under the conditions used by Limaye[4] in the case of 7-acetoxy-4-methyl-coumarin, and find that the acetyl group migrates to the ring in the 8 position. The other possible position for migration is 6, but the coumarins having this constitution have already been synthesised by the authors (in the press) from resacetophenone and respective cyclic-β-ketonic esters, and are found to be quite different.

When the cyclic-β-ketonic esters are compared with their open-chain confreres like acetoacetic esters, it is found that the former are actually more reactive than the latter, so far as the coumarin formation is concerned, although the cyclic esters can be looked upon as monosubstituted acetoacetic esters where one of the hydrogens of the methylene group, and one of the hydrogens of the methyl group are replaced by $-CH_2 \cdot CH_2-$ (in the case of cyclopentanone ester) and $-CH_2-CH_2-CH_2$ groups (in the case of cyclohexanone esters). This is possibly due to the highly enolic character of the cyclic-β-ketonic esters. The sluggishness of 6-methylcyclohexanone-2-carboxylate as compared with its 5-methyl- and 4-methyl-analogues can be attributed to the steric hindrance offered by the methyl group which is in the *ortho*-position to the enolic hydroxyl. Moreover, whereas the coumarins from dihydric and trihydric phenols obtained from 4-methyl and 5-methyl-cyclohexanone-2-carboxylates can be methylated by dimethyl sulphate and alkali, those obtained from 6-methylcyclohexanone-2-carboxylate cannot be methylated under this condition with the exception of the coumarin from resorcinol.

The nomenclature proposed in Part I of this series has been followed throughout, and in accordance with it, the coumarins from *trans*-β-decalone-3-carboxylate have been named *trans*-octalino-(2′ : 3′ : 4 : 3)-coumarin (I).



I

Experimental.

(*A*) *Coumarins from 4-methylcyclohexanone-2-carboxylate.*

7-Hydroxy-4′-methylcyclohexeno-(1′ : 2′ : 4 : 3)*-coumarin.*—A cooled solution of resorcinol (2·5 g.) and 4-methylcyclohexanone-2-carboxylate

(3·5 g.) in concentrated sulphuric acid (16 c.c.) was left overnight at the ordinary temperature. The solid obtained by pouring the mixture over ice, crystallised from dilute alcohol in flat needles melting at 217° C. It dissolved in alkali with a slight yellow colour and blue fluorescence. Concentrated sulphuric acid dissolved it to a colourless solution giving violet fluorescence. (Found : C, 72·8 ; H, 6·0 ; $C_{14}H_{14}O_3$ requires C, 73·0 ; H, 6·1 per cent.)

The *acetyl derivative* obtained by heating the coumarin (0·5 g.) with acetic anhydride (5 c.c.) in presence of a few drops of pyridine for 4 hours, crystallised from alcohol in long needles melting at 176° C. (Found : C, 70·4 ; H, 6·0 ; $C_{16}H_{16}O_4$ requires C, 70·6 ; H, 5·9 per cent.)

The *methyl ether* prepared by shaking the 5 per cent. alkaline solution of the coumarin (0·5 g.) with dimethyl sulphate (2 c.c.) crystallised from alcohol in long, fine needles melting at 123° C. (Found : C, 73·5 ; H, 6·7 ; $C_{15}H_{16}O_3$ requires C, 73·8 ; H, 6·6 per cent.)

7-Hydroxy-8-acetyl-4′-methylcyclohexeno-(1′ : 2′ : 4 : 3)- coumarin.—An intimate mixture of 7-acetoxy-4′-methylcyclohexeno-(1′ : 2′ : 4 : 3) coumarin (2 g.) and anhydrous aluminium chloride (5 g.) was heated in a round-bottom flask fitted with an air condenser at the temperature of 140° C. for an hour. The cooled mixture was decomposed with ice-cold hydrochlorice acid, and the resulting solid was purified through 5 per cent. sodium carbonate solution. The solid obtained on the addition of concentrated hydrochloric acid crystallised from dilute alcohol in fine, silky needles melting at 135° C. Its alcoholic solution gave reddish-violet coloration with ferric chloride. (Found : C, 70·3 ; H, 6·1 ; $C_{16}H_{16}O_4$ requires C, 70·6 ; H, 5·9 per cent.)

Its *semicarbazone* prepared by heating its alcoholic solution with semicarbazide acetate for 15 minutes, crystallised from alcohol in small plates, melting at 236° C. (Found : C, 61·7 ; H, 5·9 ; $C_{17}H_{19}O_4N_3$ requires C, 62·0 ; H, 5·8 per cent.)

7 : 8-Dihydroxy-4′-methylcyclohexeno-(1′ : 2′ : 4 : 3)-coumarin, was similarly obtained from pyrogallol (2·5 g.) and concentrated sulphuric acid (12 c.c.). It crystallised from dilute alcohol in small, colourless cubes melting at 256° C. Its alcoholic solution gave a deep green colour with ferric chloride. The alkaline solution showed a weak blue fluorescence, while the concentrated sulphuric acid solution was deep yellow. (Found : C, 68·1 ; H, 5·9 ; $C_{14}H_{14}O_4$ requires C, 68·3 ; H, 5·7 per cent.)

The *diacetyl derivative* crystallised from dilute alcohol in fine needles, melting at 179° C. (Found : C, 65·5 ; H, 5·6 ; $C_{18}H_{18}O_4$ requires C, 65·5 ; H, 5·5 per cent.)

The *dimethyl ether* crystallised from dilute alcohol in pointed needles, melting at 154° C. (Found : C, 69·9 ; H, 6·5 ; $C_{16}H_{18}O_4$ requires C, 70·0 ; H, 6·6 per cent.)

4'-*Methylcyclohexeno*-(1' : 2' : 4 : 3)-1 : 2-*α-naphtha-pyrone* prepared from α-naphthol crystallised from rectified alcohol in flat needles melting at 198° C. (Found : C, 81·5 ; H, 6·0 ; $C_{18}H_{16}O_2$ requires C, 81·8 ; H, 6·1 per cent.)

5-*Hydroxy*-7-*methyl*-4'-*methylcyclohexeno*-(1' : 2' : 4 : 3)-*coumarin*.—A mixture of orcinol (2 g.), the ester (3 g.), phosphorus oxychloride (1 c.c.) and dry benzene (10 c.c.) was heated on a water-bath for one hour under reflux. The residue after the removal of benzene was crystallised from dilute alcohol, when tiny white plates, melting at 250° C., were obtained. Its solution in dilute alkali was yellow, and non-fluorescent. (Found : C, 73·6 ; H, 6·4 ; $C_{15}H_{16}O_3$ requires C, 73·8 ; H, 6·6 per cent.)

The *acetyl derivative* crystallised from dilute alcohol in long, fine needles melting at 185° C. (Found : C, 71·2 ; H, 6·4 ; $C_{17}H_{18}O_4$ requires C, 71·3 ; H, 6·3 per cent.)

The *methyl ether* crystallised from dilute alcohol in long, fine needles melting at 140° C. (Found : C, 74·2 ; H, 7·2 ; $C_{16}H_{18}O_3$ requires C, 74·4 ; H, 7·0 per cent.)

5 : 7-*Dihydroxy*-4'-*methylcyclohexeno*-(1' : 2' : 4 : 3)-*coumarin*, was similarly obtained from phloroglucinol (2·6 g.), the ester (3·4 g.) and $POCl_3$ (2 c.c.) and crystallised from chloroform in plates melting at 265° C. Its alkaline solution was yellow and non-fluorescent. (Found : C, 68·2 ; H, 5·8 ; $C_{14}H_{14}O_4$ requires C, 68·3 ; H, 5·7 per cent.)

The *diacetyl derivative* crystallised from dilute alcohol in long prisms melting at 128° C. (Found : C, 65·3 ; H, 5·5 ; $C_{18}H_{18}O_6$ requires C, 65·5 ; H, 5·5 per cent.)

The *dimethyl ether* crystallised from dilute alcohol in tiny plates melting at 133° C. (Found : C, 69·8 ; H, 6·4 ; $C_{16}H_{18}O_4$ requires C, 70·0 ; H, 6·6 per cent.)

(*B*) *Coumarins from* 5-*methylcyclohexanone*-2-*carboxylate*.

7-*Hydroxy*-5'-*methylcyclohexeno*-(1' : 2' : 4 : 3)-*coumarin*, prepared from resorcinol, crystallised from dilute alcohol in fine, colourless needles melting at 202° C. Its solution in concentrated sulphuric acid gave a violet fluorescence. The alkaline solution was faint yellow and had a blue floures-cence. (Found : C, 72·7 ; H, 6·2 ; $C_{14}H_{14}O_3$ requires C, 73·0 ; H, 6·1 per cent.)

The *acetyl derivative* crystallised from dilute alcohol in colourless plates, melting at 136° C. (Found : C, 70·3 ; H, 6·1 ; $C_{16}H_{16}O_4$ requires C, 70·6 ; H, 5·9 per cent.)

The *methyl ether* crystallised from dilute alcohol in small needles melting at 118° C. (Found : C, 73·6 ; H, 6·8 ; $C_{15}H_{16}O_3$ requires C, 73·8 ; H, 6·6 per cent.)

7-*Hydroxy*-8-*acetyl*-5′-*methylcyclohexeno*-(1′ : 2′ : 4 : 3)-*coumarin*, obtained by the Fries' Transformation of 7-acetoxy-5′-methylcyclohexeno-(1′ : 2′ :4 :3)-coumarin in the usual way, crystallised from dilute alcohol in fine, silky needles melting at 142° C. Its alcoholic solution gave reddish-violet coloration with ferric chloride. (Found : C, 70·4 ; H, 6·0 ; $C_{16}H_{16}O_4$ requires C, 70·6 ; H, 5·9 per cent.)

The *semicarbazone* was a microcrystalline solid melting at 232° C.

5′-*Methylcyclohexeno*-(1′ : 2′ : 4 : 3)-1 : 2-*α-naphtha-pyrone*, prepared from α-naphthol, crystallised from dilute alcohol in needles melting at 173° C. (Found : C, 81·7 ; H, 6·3 ; $C_{18}H_{16}O_2$ requires C, 81·8 ; H, 6·1 per cent.)

7 : 8-*Dihydroxy*-5′-*methylcyclohexeno*-(1′: 2′ : 4 : 3)-*coumarin*, obtained from pyrogallol, crystallised from dilute alcohol in tiny plates melting at 231° C. Its solution in dilute alkali was yellow and fluorescent (blue). The alcoholic solution gave deep green colour with ferric chloride. (Found : C, 68·0 ; H, 5·8. Calc. for $C_{14}H_{14}O_4$: C, 68·3 ; H, 5·7 per cent.)

The *diacetyl derivative* crystallised from dilute alcohol in small needles melting at 214° C. (Found : C, 65·2 ; H, 5·7 ; $C_{18}H_{18}O_6$ requires C, 65·5 ; H, 5·5 per cent.)

The *dimethyl ether* crystallised from hexane in needles melting at 123° C. (Found : C, 69·8 ; H, 6·6 ; $C_{16}H_{18}O_4$ requires C, 70·0 ; H, 6·6 per cent.)

5-*Hydroxy*-7-*methyl*-5′-*methylcyclohexeno*-(1′ : 2′ : 4 : 3)-*coumarin*, *prepared* from orcinol, crystallised from dilute alcohol in colourless needles melting at 260° C. [Sen and Basu (*loc. cit*) give 249° C]. Its alkaline solution was yellow and non-fluorescent. (Found : C, 73·5 ; H, 6·8. Calc. for $C_{15}H_{16}O_3$: C, 73·8 ; H, 6·6 per cent.)

The *acetyl derivative* crystallised from dilute alcohol in fine needles melting at 134° C. (Found : C, 71·0 ; H, 6·2 ; $C_{17}H_{18}O_4$ requires C, 71·3 ; H, 6·3 per cent.)

The *methyl ether* crystallised from hexane in flat needles melting at 98° C. (Found : C, 74·1 ; H, 7·1 ; $C_{16}H_{18}O_3$ requires C, 74·4 ; H, 7·0 per cent.)

5 : 7-*Dihydroxy*-5′-*methylcyclohexeno*-(1′: 2′: 4 : 3)-*coumarin*, prepared from phloroglucinol crystallised from chloroform in tiny plates melting at 262° C. It dissolved in alkali with a yellow colour and no fluorescence. (Found : C, 68·0 ; H, 5·9. Calc. for $C_{14}H_{14}O_4$: C, 68·3 ; H, 5·7 per cent.)

The *diacetyl derivative* crystallised from dilute alcohol in small needles melting at 117° C. (Found : C, 65·4 ; H, 5·4 ; $C_{18}H_{18}O_6$ requires C, 65·5 ; H, 5·5 per cent.)

(*C*) *Coumarins from 6-methylcyclohexanone-2-carboxylate.*

This ester condenses with phenols in the presence of $POCl_3$ only.

7-Hydroxy-6'-methylcyclohexeno-(1' : 2' : 4 : 3)-coumarin.—A mixture of resorcinol (2·4 g.), the ester (4·5 g.), $POCl_3$ (2 c.c.), and dry benzene (10 c.c.) was heated under reflux on water-bath for two hours. Benzene was decanted off, and the residue was extracted with three lots of benzene (15 c.c. each time). The solvent was removed from the combined extracts, and the residue crystallised from alcohol in thick, lustrous plates melting at 205° C. The yellow alkaline solution showed a blue fluorescence while its solution in concentrated sulphuric acid was colourless but gave violet fluorescence. (Found : C, 72·7 ; H, 5·9 ; $C_{14}H_{14}O_3$ requires C, 73·0 ; H, 6·1 per cent.)

The *acetyl derivative* crystallised from dilute alcohol in needles, melting at 174° C. (Found : C, 70·5 ; H, 6·1 ; $C_{16}H_{16}O_4$ requires C, 70·6 ; H, 5·9 per cent.)

The *methyl ether* crystallised from alcohol in colourless needles, melting at 112° C. (Found : C, 73·6 ; H, 6·5 ; $C_{15}H_{16}O_3$ requires C, 73·8 ; H, 6·6 per cent.)

7 : 8-Dihydroxy-6'-methylcyclohexeno-(1' : 2' : 4 : 3)-coumarin, obtained from pyrogallol, crystallised from alcohol in tiny plates melting at 227° C. (Found : C, 68·0 ; H, 5·8 ; $C_{14}H_{14}O_4$ requires C, 68·3 ; H, 5·7 per cent.)

The *diacetyl derivative* crystallised from dilute alcohol in prisms melting at 140° C. (Found : C, 65·2 ; H, 5·5 ; $C_{18}H_{18}O_6$ requires C, 65·5 ; H, 5·5 per cent.)

5 : 7-Dihydroxy-6'-methylcyclohexeno-(1' : 2' : 4 : 3)-coumarin, obtained from phloroglucinol, crystallised from alcohol in small plates melting, at 275°C. (Found : C, 68·4 ; H, 5·7 ; $C_{14}H_{14}O_4$ requires C, 68·3 ; H, 5·7 per cent.)

The *diacetyl derivative* crystallised from dilute alcohol in needles melting at 127° C. (Found : C, 65·4 ; H, 5·7 ; $C_{18}H_{18}O_6$ requires C, 65·5 ; H, 5·5 per cent.)

7-Hydroxy-6-ethyl-6'-methylcyclohexeno-(1' : 2' : 4 : 3)-coumarin, obtained from 4-ethylresorcinol, crystallised from alcohol in rhombic needles, melting at 232° C. Its colourless solution in concentrated sulphuric acid gave violet fluorescence, while the yellow, alkaline solution gave blue fluorescence. (Found : C, 74·3 ; H, 7·2 ; $C_{16}H_{18}O_3$ requires C, 74·4 ; H, 7·0 per cent.)

The *acetyl derivative* crystallised from alcohol in lustrous plates, melting at 118° C. (Found : C, 71·8 ; H, 6·9 ; $C_{18}H_{20}O_4$ requires C, 72·0 ; H, 6·7 per cent.)

The *methyl ether* crystallised from dilute alcohol in long lustrous plates melting at 109° C. (Found : C, 74·7 ; H, 7·7 ; $C_{17}H_{20}O_3$ requires C, 75·0 ; H, 7·6 per cent.)

5-*Hydroxy*-7-*methyl*-6′-*methylcyclohexeno*-(1′ : 2′ : 4 : 3)-*coumarin*, obtained from orcinol, crystallised from alcohol in tiny plates melting at 235° C. Its alkaline solution was yellow and devoid of fluorescence. (Found : C, 73·5 ; H, 6·7 ; $C_{15}H_{16}O_3$ requires C, 73·8 ; H, 6·6 per cent.)

The *acetyl derivative* crystallised from alcohol in tiny needles, melting at 124° C. (Found : C, 71·0 ; H, 6·5 ; $C_{17}H_{18}O_4$ requires C, 71·3 ; H, 6·3 per cent.)

6′-*Methylcyclohexeno*-(1′ : 2′ : 4 : 3)-1 : 2-α-*naphthapyrone*, *prepared from* α-naphthol, crystallised from dilute alcohol in long needles melting at 112° C. (Found : C, 81·6 ; H, 6·2 ; $C_{18}H_{16}O_2$ requires C, 81·8 ; H, 6·1 per cent.)

(*D*) *Coumarins from trans-β-decalone-3-carboxylate.*

7-*Hydroxy-trans-octalino*-(2′ : 3′ : 4 : 3)-*coumarin*, prepared from resorcinol and the ester, crystallised from rectified spirit in pale-brown plates melting at 245° C. Its yellow, alkaline solution gave blue fluorescence. The colourless solution in concentrated sulphuric acid gave violet fluorescnece. Ferric chloride gave green colouration to its alcoholic solution. (Found : C, 75·4 ; H, 6·8 ; $C_{17}H_{18}O_3$ requires C, 75·4 ; H, 6·7 per cent.)

The *acetyl derivative* crystallised from alcohol in fine colourless needles, melting at 192° C. (Found : C, 72·8 ; H, 6·6 ; $C_{19}H_{20}O_4$ requires C, 73·1 ; H, 6·4 per cent.)

The *methyl ether* crystallised from alcohol in colourless plates melting at 178° C. (Found : C, 75·9 ; H, 7·1 ; $C_{18}H_{20}O_3$ requires C, 76·1 ; H, 7·0 per cent.)

7-*Hydroxy*-8-*acetyl-trans-octalino*-(2′ : 3′ : 4 : 3)-*coumarin*, was prepared by the Fries' Transformation of 7-acetoxy-*trans*-octalino-(2′ : 3′ : 4 : 3)-coumarin, and crystallised from alcohol in silky needles melting at 167° C. Its alcoholic solution gave reddish-violet colour with ferric chloride. (Found : C, 72·9 : H, 65 ; $C_{19}H_{20}O_4$ requires C, 73·1 ; H, 6·4 per cent.)

The *semicarbazone* crystallised from alcohol in small plates melting at 258° C.

Trans-octalino-(2′ : 3′ : 4 : 3)-1 : 2-α-*naphthapyrone*, obtained from α-naphthol, crystallised from acetic acid in pointed needles melting at 222° C. (Found : C, 82·6 ; H, 67 ; $C_{21}H_{20}O_2$ requires C, 82·9 ; H, 6·6 per cent.)

7 : 8-*Dihydroxy-trans-octalino*-(2′ : 3′ : 4 : 3)-*coumarin*, obtained from pyrogallol, crystallised from alcohol in prismatic needles melting at 267° C. The coumarin forms a very sparingly soluble sodium salt, and cannot be methylated by dimethyl sulphate. Its alcoholic solution gives deep bluish green coloration with ferric chloride, while concentrated sulphuric acid dissolves it with a yellow colour. (Found : C, 71·0 ; H, 6·5 ; $C_{17}H_{18}O_4$ requires C, 71·3 ; H, 6·3 per cent.)

The *di-acetyl derivative* crystallised from alcohol in fine needles melting at 200° C. (Found : C, 68·0 ; H, 5·9 ; $C_{21}H_{22}O_6$ requires C, 68·1 ; H, 6·0 per cent.)

5-*Hydroxy-7-methyl-trans-octalino*-(2′ : 3′ : 4 : 3)-*coumarin*, prepared from orcinol, was a microcrystalline powder melting at 315° C. It could not be satisfactorily crystallised from any solvent. Its alkaline solution was yellow and non-fluorescent. It could not be methylated by dimethyl sulphate and alkali. (Found : C, 75·8 ; H, 7·2 ; $C_{18}H_{20}O_3$ requires C, 76·1 ; H, 7·0 per cent.)

The *acetyl derivative* crystallised from alcohol in tiny needles melting at 184° C. (Found : C, 73·4 ; H, 6·5 ; $C_{20}H_{24}O_3$ requires C, 73·6 ; H, 6·7 per cent.)

5 : 7-*Dihydroxy-trans-octalino*-(2′ : 3′ : 4 : 3)-*coumarin*, obtained from phloroglucinol, crystallised from alcohol in small plates melting at 265° C. Its alcoholic solution gave green coloration with ferric chloride. The yellow, alkaline solution was devoid of fluorescence. It could not be methylated by sulphate and alkali. (Found : C, 71·1 ; H, 6·4 ; $C_{17}H_{18}O_4$ requires C, 71·3 ; H, 6·3 per cent.)

The *diacetyl derivative* crystallised from alcohol in needles melting at 173° C. (Found : C, 67·9 ; H, 6·2 ; $C_{21}H_{22}O_6$ requires C, 68·1 ; H, 6·0 per cent.)

Summary.

Coumarins have been prepared from alkylcyclo-hexanone-2-carboxylates and *trans*-β-decalone-3-carboxylate by condensing various dihydric and trihydric phenols either in the presence of concentrated sulphuric acid or phosphorus oxychlorid. The Fries' Transformation of the 7-acetoxy-derivatives of the various coumarins has been studied with the purpose of comparing the 7-hydroxy-8-acetyl derivatives with their 7-hydroxy-6-acetyl isomers.

REFERENCES.

1. Z. Ahmad and Desai, *Proc. Ind. Acad. Sci.*, (A), 1937, **5**, 277.
2. Sen and Basu, *J. Ind. Chem. Soc.*, 1928, **5**, 467.
3. Z. Ahmad and Desai, *Proc. Ind. Acad. Sci.*, 1937, **6**, 6.
4. Limaye, *Ber.*, 1932, **65**, 375 ; 1934, **67**, 12.
5. ———— and Gangal, *Rasayanam*, 1936, **1**, 64, etc.

ON LINEAR TRANSFORMATIONS OF BOUNDED SEQUENCES—II.

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Part II.

		Page
§ 7.	General Remarks	20
§ 8.	Six theorems on very general combinations of direct and inverse transformations (T)	20
§ 9.	On combinations of inverse transformations	29
§ 10.	On the properties of a subclass of (T)	31
§ 11.	Two theorems applicable for a special subclass of (T) ..	32
§ 12.	On an integral equation	35

§ 7. *General Remarks.*

Theorems II and III of Part I dealt completely with the way in which direct T's combine, and the equivalence of combinations of T's to other transformations defined by matrices. Theorem IV and its complement dealt with the simplest case of combinations of direct T's and inverse T^{-1}'s. In this part we propose to prove some very general theorems on such combinations, in (8) and (9). (10) deals with a subclass of T designated $\overline{T}$, whose inverses (T^{-1}) behave very much like any direct T ; so that Theorems II and III of Part I characterize completely the way in which $\overline{T}^{-1}$ or a product $(\overline{T}_1^{-1} \cdot \overline{T}_2^{-1} \cdot \overline{T}_k^{-1})$ can combine with any T's. In (8) and (9), we will notice that in all the theorems the sequence (x_n), on which the transformations are applied will be at least a null sequence. In (11) two theorems applicable to bounded sequences, for special subclass of T's are proved. (12) deals with the solution of an integral equation, an adaptation to the continuous variable of Theorem IV of Part I.

As in Part I the matrix defining a T will be denoted by $\| a_{m,n} \|$ where $a_{m,n}$ is characterized by the four conditions of (2·1), and the matrix defining T^{-1} by $\| \beta_{m,n} \|$. The numbering of theorems here is in continuation of the theorems of Part I.

§ 8. *General Theorems.*

Theorem V : Let S be a transformation defined by $\|c_{m,n}\|$ such that $c_{m,n} = 0$ $n < m$, and R the product of a number of direct T's, *i.e.*, $R = (T_1 T_2 \cdots T_k)$,

defined by $\| d_{m,n} \| = \| a^1_{m,n} \| \cdot \| a^2_{m,n} \| \cdots \| a^k_{m,n} \|$, where $\| a^k_{m,n} \|$ defines T_p and let $\| h_{m,n} \| = \| d_{m,n} \| \cdot \| c_{m,n} \|$. If the set of series $\sum_{n=\infty}^{n=\infty} c_{m,n} y_n$ converge uniformly for all m, then

(1) $(R) \cdot [S(y_n)] = (R \cdot S)(y_n)$; (2) $\sum_{n=\infty}^{n=\infty} h_{m,n} y_n$ converge uniformly for all m : (3) the sequence $S(y_n)$ is a null one.

Lemma 1. $\sum_{p=\infty}^{p=\infty} | d_{n,n+p} | \leqslant k$ for all n,

Proof :— $d_{n,n+p} = \Sigma \cdot \Sigma\Sigma a^1_{n,n+p_1} \cdot a^2_{n+p_1,n+p_2} \cdot \quad a^k_{n+p_{k-1},n+p}$.

Hence $\sum_{p=\infty}^{p=\infty} |d_{n,n+p}| \leqslant \sum_{p=\infty}^{p=\infty} (\Sigma \cdots \Sigma |a^1_{n,n+p_1}| \cdots |a^k_{n+p_{k-1},n+p}|)$

$= \sum_{p_1=\infty}^{p_1=\infty} |a^1_{n,n+p_1}| \cdots \sum_{p_{k-1}=\infty}^{p_{k-1}=\infty} |a^{k-1}_{n+p_{k-2},n+p_{k-1}}| \cdot \sum_{p=\infty}^{p=\infty} |a^k_{n+p_{k-1},n+p}|$.

Now by condition (d) of 2·1 $\sum_{p=0}^{p=\infty} |a^r_{n,n+p}| \leqslant 2$.

Hence $\sum_{p=\infty}^{p=\infty} |d_{n,n+p}| \leqslant 2^k \cdot = k$. [8·1]

Proof of Theorem V :—Let $\epsilon > 0$, N_0 so chosen that for all $A \geqslant N_0$ and for all $m \geqslant 0$

$\left| \sum_{n=A}^{\infty} c_{m,n} y_n \right| \leqslant \epsilon$. Let m be a fixed integer, and A_0 another fixed integer such that $A_0 > N_0$ and $A_0 > m$.

Let $z_n = \sum^{\infty} c_{n,p} \cdot y_p = S(y_n)$.

Then

$$z_m = \sum_{n=\infty}^{n=\infty} c_{m,n} y_n = \sum_{n=\infty}^{n=A_0} + \sum_{n=A_0+1}^{\infty} = \sum_{n=\infty}^{n=A_0} + \theta_m \epsilon.$$

and $z_{m+r} \sum_{n=\infty}^{n=A_0} c_{m+r,n} y_n + \theta_{m+r} \cdot \epsilon$

for $m + r \leqslant A_0$;

and $z_{A_0+k} = \sum_{n=A_0+k}^{n=\infty} c_{A_0+k,n} \cdot y_n = \theta_{A_0+k} \cdot \epsilon$, [8·2]

where $-1 \leqslant \theta_p \leqslant 1$.

Hence $|z_{A_0+k}| \leqslant \epsilon$ for all $k \geqslant 0$ proving (3) of Theorem V. [8·3]

Now $R(z_m) = \sum_{p=\infty}^{p=\infty} d_{m,p} z_p = \sum_{p=\infty}^{p=A_0} + \sum_{p=A_0+1}^{\infty} = B_1 + B_2$. [8·4]

By (8·1) and (8·3) $|B_2| \leqslant k\epsilon$.

By (8·2) $B_1 = \sum^{p=A_0} \cdot d_{m,p} \cdot \left(\sum^{r=A_0} c_{p,r}\, y_r + \theta_p\, \epsilon \right) =$

$$\sum^{p=A_0} d_{m,p} \cdot \sum^{r=A_0} c_{p,r} \cdot y_r + \epsilon \sum^{p=A_0} \theta_p \cdot d_{m,p}$$

$$= \sum^{r=A_0} (\Sigma d_{m,p} \cdot c_{p,r})\, y_r + \theta' k \cdot \epsilon. \qquad -1 \leqslant \theta' \leqslant 1.$$

$$= \sum^{r=A_0} h_{m,r} \cdot y_r + \theta' k \epsilon.$$

Hence $\sum^{p=\infty} d_{m,p} \cdot z_p = \sum^{r=A_0} h_{m,r}\, y_r + \theta'' \cdot 2k \cdot \epsilon \quad -1 \leqslant \theta'' \leqslant 1.$ [8·5]

Making $A_0 \to \infty$. We have

$$\sum^{p=\infty} d_{m,p}\, z_p = \sum^{r=\infty} h_{m,r}\, y_r \qquad \text{or} \qquad [8\cdot6]$$

$$R(z_n) = (R)\,[S(y_n)] = (RS)(y_n). \qquad [8\cdot7]$$

From (8·5) and (8·6) we get $\left| \sum_{r=A_0+1}^{\infty} h_{m,r}\, z_r \right| \leqslant 2k\epsilon$ proving (2) of theorem V. [8·8]

THEOREM VI: Let S be any transformation defined by $\| c_{m,n} \|$ such that $c_{m,n} = 0$ for $n < m$, and R_1 the product of a number of direct transformations, *i.e.*, $R_1 = (T_{s_1} T_{s_2} \cdot T_{s_\rho})$ defined by $\| d_{m,n} \| = \| a^{s_1}{}_{m,n} \| \cdots \| a^{s_\rho}{}_{m,n} \|$, and R_2 the product of number of inverse transformations, *i.e.*, $R_2 = (T_1^{-1} T_2^{-1} T_k^{-1})$ defined by $\| \bar{\beta}_{mn} \| = \| \beta^1{}_{m,n} \| \cdots \| \beta^k{}_{m,n} \|$. where $\| \beta^s{}_{m,n} \|$ defines (T_s^{-1}). Let b_p be the upper bound of $\bar{\beta}_{n,n+p}$ for all n and $\sum_0^{p=n} b_p = B_n$. If $\left| \sum_{n=A}^{\infty} c_{m,n}\, y_n \right| = 0\left(\frac{1}{B_A}\right)$ for all m and for all sufficiently large A, then

$(R_1 R_2)\,[S(y_n)] = (R_1 R_2 S)(y_n)$ when the latter exists.

Proof:—Let m_0 be any positive integer, and A_0 sufficiently large and $A_0 > m_0$.

Let $z_n = S(y_n)$.

Then $z_{m_0} = \sum^{n=\infty} c_{m_0,n} \cdot y_n = \sum^{n=A_0-1} + \sum_{A_0}^{\infty} = \sum^{n=A_0-1} + \theta_{m_0} \cdot \frac{\epsilon_{A_0}}{B_{A_0}}$

$$z_{m_0+r} = \sum^{n=A_0-1} c_{m_0+r,n}\, y_n + \theta_{m_0+r} \cdot \frac{\epsilon_{A_0}}{B_{A_0}} \qquad [8\cdot9]$$

for $m_0 + r \leqslant A_0 - 1$; $-1 \leqslant \theta_p \leqslant 1$.

Let $\| \gamma_{mn} \| = \| d_{m,n} \| \cdot \| \bar{\beta}_{m,n} \|$.

Then $\sum_{n=m_0}^{n=A_0-1} \gamma_{m_0,n} z_n = \sum^{n=A_0-1} \gamma_{m_0 n} \cdot \left(\sum^{p=A_0-1} c_{n,p} y_p + \theta_n \frac{\epsilon_{A_0}}{B_{A_0}} \right)$

$$= \sum^{p=A_0-1} (\Sigma \gamma_{m_0,n} c_{n,p}) y_p + \frac{\epsilon_{A_0}}{B_{A_0}} \sum^{n=A_0-1} \gamma_{m_0 n} \theta_n = B_1 + B_2$$

$$|B_2| \leqslant \frac{\epsilon_{A_0}}{B_{A_0}} \cdot \sum^{n=A_0-1} |\gamma_{m_0 n}|, \text{ and } \gamma_{m_0 n} = \sum_{n_1=m_0}^{n_1=n} d_{m_0 n_1} \bar{\beta}_{n_1,n}$$

Hence $|\gamma_{m_0 n}| \leqslant \sum_{n_1=m}^{n_1=n} |d_{m\, n_1}|\, b_{n-n_1}$ and $\sum_{n=m_0}^{n=A_0-1} |\gamma_{m_0 n}| = \sum_{n=m_0}^{n=A_0-1} \sum_{n_1=m_0}^{n_1=n} |d_{m_0 n_1}| b_{n-n_1}$

$$= \sum_{k=0}^{A_0-1-m_0} b_k \sum_{n=m_0}^{A_0-1-\mu} |d_{m_0 n}| \leqslant k \cdot B_{A_0-1-m_0} \text{ where } \sum_{n=m_0}^{\infty} |d_{m_0 n}| \leqslant k \text{ by (8·1)}$$

Hence $$|B_2| \leqslant k \cdot \frac{B_{A_0-1-m_0}}{B_{A_0}} \cdot \epsilon_{A_0} \leqslant k \cdot \epsilon_{A_0}.$$

Hence $$\sum^{n=A_0-1} \gamma_{m_0 n} z_n = \sum^{p=A_0-1} (\Sigma\, \gamma_{m_0 n} \cdot c_{n,p})\, y_p + \theta k \epsilon_{A_0}$$

$$= \sum^{p=A_0-1} \gamma^1{}_{m_0 p}\, y_p + \theta k \epsilon_{A_0},$$

where $\| \gamma^1{}_{m\,n} \| = \| \gamma_{m,n} \| \cdot \| c_{m,n} \|$.

If the series $\sum^{\infty} \gamma^1{}_{m_0 p}\, y_p$ converges, *i.e.*, $(R_1 R_2 S)\ (y_n)$ exists, then making $A_0 \to \infty$ we have

$$\sum^{n=\infty} \gamma_{m_0 n} z_n = \sum^{p=\infty} \gamma_{m_0 p}\, y_p \qquad [8\cdot 10]$$

i.e., $(R_1 R_2)\ [S\ (y_n)] = (R_1 R_2 S)\ (y_n)$ when the latter exists.

THEOREM VII: Let $R_1 = (T_{q_1} T_{q_2} T_{q_r})$ defined by $\| d_{m,n} \|$; $R_2 = (T_{s_1} T_{s_2} T_{s_\rho})$ defined by $\| e_{m,n} \|$

$$[\| d_{mn} \| = \| a^{a_1}_{m,n} \| \cdots \| a^{a_r}_{m,n} \|;\ \| e_{mn} \| = \| a^{s_1}_{m,n} \| \cdots \| a^{s_\rho}_{m,n} \|.]$$

and $I = (T_1{}^{-1} T_2{}^{-1} T_k{}^{-1})$ defined by $\| \bar{\beta}_{mn} \| = \| \beta^1_{m,n} \| \cdots \| \beta^k_{m,n} \|$.

Let $S\ (R_i\, I\, R_2)$ be defined by $\| \gamma_{mn} \| = \| d_{m,n} \| \cdot \| \bar{\beta}_{m,n} \| \cdot \| e_{m,n} \|$.

Let the upper bound of $\bar{\beta}_{n,n+p}$ be b_p, and $\sum_{p=0}^{n} b_p = B_n$.

If $y_n = 0\left(\frac{1}{B_n{}^{1+\delta}}\right)$ in case B_n diverges, or $y_n = 0\ (1)$ when B_n converges, then $(1) \sum^{n=\infty} |\gamma_{m,n}\, y_n|$ converges uniformly for all m;

(2) the terms of the product S can be associated in any manner and the resultants of the operations on the sequence y_n are all equal to S (y_n)

[for example $(T_{q_1} T_{q_2} T_{q_{r_1}})(T_{q_{r_1+1}} \cdot\cdot T_{q_r}) \cdot (\cdot T_1^{-1} \cdot\cdot T_l^{-1})(T_{l+1}^{-1} \cdot\cdot T_k^{-1})$

$(T_{s_1} \cdot T_{s_p^1})(T_{s_p^1+1} \cdot\cdot T_{s_p}) (y_n) = S(y_n)$.]

Lemma I: $|\gamma_{m,m+p}| \leqslant \sum_r \sum_k |d_{m,m+r}| \cdot \bar{\beta}_{m+r,m+r+k} \cdot |e_{m+r+k,m+p}|$

$$\leqslant \sum_{k=0}^{k=p} b_k \cdot \sum_{r=0}^{r=p-k} |d_{m,m+r}| \cdot |e_{m+r+k,m+p}| \qquad [8\cdot11]$$

Lemma II: Let the terms of R_1 be associated in any manner.

i.e., Let $R_1 = (T_{q_1} \cdot\cdot T_{q_{r_1}}) \cdot (T_{q_{r_1+1}} \cdot\cdot T_{q_{r_2}}) \cdots (T_{q_{r_{p-1}+1}} \cdots T_{q_r})$

$= R_1^1 \cdot R_2^1 \cdots R_p^1$.

and let R_1^1 be defined by $\| d^1_{m,n} \|$, R_2^1 by $\| d^2_{m,n} \|$ and so on.

Let f^1_{mn} = absolute value of d^1_{mn}. *i.e.* $= |d^1_{m,n}|$ etc.

If $\| \bar{d}_{mn} \| = \| f^1_{m,n} \| \cdot \| f^2_{m,n} \| \cdot\cdot \| f^p_{m,n} \|$.

Then $$\sum_{n=0}^{\infty} \bar{d}_{m,n} \leqslant 2^r. \qquad [8\cdot12)$$

Proof:— Since by $2\cdot1$ $\sum_{n=0}^{n=\infty} |a_{m,n}| \leqslant 2$ for all m

$$\sum_{n=0}^{n=\infty} f^1_{m,n} \leqslant 2^{r_1}$$

$$\sum_{n=0}^{n=\infty} f^2_{m,n} \leqslant 2^{r_2 - r_1} \cdot\cdot$$

and $$\sum_{n=0}^{n=\infty} f^p_{m,n} \leqslant 2^{r - r_{p-1}} \qquad \text{by } 8\cdot1.$$

Hence $$\sum_{n=0}^{\infty} \bar{d}_{m,n} \leqslant 2^{r_1} \cdot 2^{r_2 - r_1} \cdots 2^{r - r_{p-1}} = 2^r. \qquad [8\cdot13]$$

Proof of (1): Let $A > 0$ be any fixed integer and let B_n diverge; and let m be any positive integer. Let $|y_n| \leqslant \frac{K}{B_n^{1+\delta}}$ by hypothesis. Consider now Case I when $m \leqslant A$, *i.e.*, $m + q = A$.

$$\sum_{n=A}^{\infty} |\gamma_{m,n}|\, |y_n| = \sum_{p=q}^{\infty} |\gamma_{m,m+p}|\, |y_{m+p}| \leqslant$$

$$K. \sum_{p=q}^{p=\infty} \frac{\sum_{k=0}^{p} b_k \cdot \sum |d_{m,m+r}| \cdot |e_{m+k+r,m+p}|}{B_{m+p}^{1+\delta}}$$

$$= K \sum_{k=0}^{\infty} b_k \cdot \sum_{r=0}^{\infty} |d_{m,m+r}| \cdot \sum_{p=q}^{\infty} \frac{|e_{m+k+r,m+p}|}{B_{m+p}^{1+\delta}} = K \cdot \sum_{k=0}^{\infty} b_k \cdot \phi(k) =$$

$$K\left(\sum^{k=A} + \sum_{A+1}^{\infty}\right)$$

$$= K(B_1 + B_2). \qquad [8\cdot14]$$

Since by 8·1 $\sum_{r=0}^{r=\infty} |e_{m,r}| \leqslant 2^p = K_2$, $\sum_{p=q}^{\infty} \frac{|e_{m+k+r,m+p}|}{B_{m+p}^{1+\delta}} \leqslant \frac{K_2}{B_{m+q}^{1+\delta}} = \frac{K_2}{B_A^{1+\delta}}$

Hence

$$B_1 \leqslant K_2 \cdot \sum^{k=A} b_k \sum_{r=0}^{\infty} \frac{|d_{m,m+r}|}{B_A^{1+\delta}} \leqslant \frac{K_2 K_1}{B_A^{1+\delta}} \sum^{k=A} b_k \text{ since } \Sigma |d_{m,m+r}| \leqslant K_1 \text{ by (8·1)}$$

$$= \frac{K_2 K_1}{B_A^{\delta}}. \qquad [8\cdot15]$$

$$B_2 = \sum_{k=1}^{\infty} b_{A+k} \cdot \sum_{r=0}^{\infty} |d_{m,m+r}| \cdot \sum_{p=q}^{\infty} \frac{|e_{m+r+A+k,m+p}|}{B_{m+p}^{1+\delta}}$$

Now $e_{m,n} = 0 \quad n < m$ and $m + q = A$.

Hence $\sum_{p=q}^{\infty} \frac{|e_{m+r+A+k,m+p}|}{B_{m+p}^{1+\delta}} = \sum_{p=r+A+k}^{\infty} \frac{|e_{m+r+A+k,m+p}|}{B_{m+p}^{1+\delta}} \leqslant \frac{K_2}{B_{m+r+A+k}^{1+\delta}}$

and $$\sum_{r=0}^{\infty} \frac{|d_{m,m+r}|}{B_{m+r+A+k}^{1+\delta}} \leqslant \frac{K_1}{B_{m+A+k}^{1+\delta}}.$$

Hence $B_2 \leqslant \sum_{k=1}^{\infty} b_{A+k} \cdot \frac{K_1 K_2}{B_{m+A+k}^{1+\delta}} \leqslant K_1 K_2 \cdot \sum_{k=1}^{\infty} \frac{b_{A+k}}{B_{A+k}^{1+\delta}} \leqslant \frac{K_1 K_2}{\delta B_A^{\delta}}$

since $$\frac{1}{B_{n-1}^{\delta}} - \frac{1}{B_n^{\delta}} \geqslant \frac{\delta b_n}{B_n^{1+\delta}}.$$

Hence $$B_1 + B_2 = 0\left(\frac{1}{B_A^{\delta}}\right) \qquad [8\cdot16]$$

Case II. $m > A$;

proceeding exactly as above we can prove for all m.

$$\sum_{n=0}^{\infty} |\gamma_{mn} y_n| = \sum_{n=m}^{\infty} |\gamma_{mn} y_n| = 0\left(\frac{1}{B_m^{\delta}}\right).$$

Hence when $m > A$

$$\sum_{n=A}^{\infty} |\gamma_{mn} y_n| = \sum_{n=m}^{\infty} |\gamma_{mn} y_n| \quad \text{since } \gamma_{mn} = 0 \quad n < m$$

and $\sum_{n=m}^{\infty} |\gamma_{mn}\, y_n| = 0\left(\frac{1}{B_m^{\delta}}\right) = 0\left(\frac{1}{B_A^{\delta}}\right)$ since $m > A$.

Hence in all cases $\sum_{n=A}^{\infty} |\gamma_{m,n}\, y_n| = 0\left(\frac{1}{B_A^{\delta}}\right)$. [8·17]

Hence (1) is proved.

With regard to (2) of Theorem VII we shall prove a particular case of the associations, the proof being the same in all other cases.

To prove $(T_{q_1} T_{q_2} T_{q_{r_1}})\,(T_{q_{r_1+1}} \cdots T_{q_r})\,(T_1^{-1} \cdots T_l^{-1})\,(T_{l+1}^{-1} \cdots T_k^{-1}) \times$
$\times (T_{s_1} \cdots T_{s_\rho^1})\,(T_{s_\rho^1+1} \cdots T_{s_\rho})\,(y_n) = (T_{q_1} \cdots T_{q_r} \cdot T_1^{-1} \cdots T_k^{-1} \cdot T_{s_1} \cdots T_{s_\rho})\,(y_n)$
$= S\,(y_n)$ [8·18]

Let $(T_{q_1} \cdots T_{q_{r_1}})$ be defined by $\| d'_{m,n} \|$, $(T_{q_{r_1+1}} \cdots T_{q_r})$ by $\| d''_{mn} \|$

$(T_1^{-1} \cdots T_l^{-1})$ by $\| \bar{\beta}'_{m,n} \|$, $(T_{l+1}^{-1} \cdots T_k^{-1})$ by $\| \beta''_{m,n} \|$.

$(T_{s_1} \cdots T_{s_\rho^1})$ by $\| e'_{m,n} \|$, $(T_{s_\rho^1+1} \cdots T_{s_\rho})$ by $\| e''_{m,n} \|$

and let $\bar{d}_{m,n} = \sum_{n_1} |d'_{m,n_1}| \cdot |d''_{n_1,n}|$

and $\bar{e}_{m,n} = \sum |e'_{m,n}| \cdot |e''_{m,n}|$.

Now $\sum_{n_1} |d'_{m,n_1}| \cdot \sum_{n_2} |d''_{n_1,n_2}| \cdot \sum_{n_3} \bar{\beta}'_{n_2,n_3} \cdot \sum_{n_4} \bar{\beta}''_{n_3,n_4} \cdot \sum_{n_5} |e'_{n_4,n_5}| \cdot \sum_{\rho} |e''_{n_5,\rho}|\,(y_\rho)$

$= \sum_{n_1} (\sum |d'_{m,n_1}|\,|d''_{n_1 n_2}|) \cdot \sum \bar{\beta}_{n_2,n_4} \cdot \sum_{n_5} (\sum |e'_{n_4,n_5}| \cdot |e''_{n_5,\rho}|)\,|y_\rho|$

$= \sum \bar{d}_{m,n_1} \cdot \sum \bar{\beta}_{n_1,n_2} \sum \bar{e}_{n_2\rho}\,|y_\rho| = \sum_{\rho}^{\rho=\infty} (\Sigma\Sigma\, \bar{d}_{m,n_1} \cdot \bar{\beta}_{n_1,n_2} \cdot \bar{e}_{n_2,\rho})\,|y_\rho|$

Since by (8·13), $\sum_{\rho=0}^{\infty} \bar{d}_{n,\rho} \leqslant K$ and $\sum \bar{e}_{n,\rho} \leqslant K^1$

exactly as in the proof of (1) of this theorem, we prove $\sum^{\rho=\infty} (\Sigma\Sigma\, d_{m,n_1} \cdot \bar{\beta}_{n_1,n_2} \cdot \bar{e}_{n_2\rho})\,|y_\rho|$ converges.

Hence

$$\sum^{n_1=\infty} d'_{m,n_1} \sum^{n_2=\infty} d''_{n_1 n_2} \cdot \sum^{n_3=\infty} \bar{\beta}'_{n_2,n_3} \cdot \sum^{n_4=\infty} \bar{\beta}''_{n_3,n_4} \cdot \sum^{n_5=\infty} e'_{n_4,n_5} \cdot \sum^{\rho=\infty} e''_{n_5\rho}\, y_\rho$$

$$= \sum^{\rho=\infty} (\Sigma\Sigma \cdots \Sigma \cdots \Sigma\Sigma\, d'_{m,n_1} \cdot d''_{n_1,n_2}\, \bar{\beta}'_{n_2,n_3}\, \bar{\beta}''_{n_3,n_4}\, e'_{n_4,n_5}\, e''_{n_5,\rho})\, y_\rho = S\,(y_n)$$

i.e., (8·18) is true. [8·19]

We will state here some of the other associations that are equivalent to $S\,(y_n)$ as they will be needed later.

$$(T_{q_1} T_{q_2} \cdots T_{q_r} T_1^{-1} \cdot\cdot T_l^{-1})\,(T_{l+1}^{-1} \cdot\cdot T_k^{-1} T_{s_1} \cdot\cdot T_{s_\rho})\,(y_n) =$$
$$(T_{q_1} T_{q_2} \cdot T_{q_r}) \cdot (T_1^{-1} \cdot\cdot T_k^{-1} T_{s_1} \cdot\cdot T_{s_\rho})\,(y_n) =$$
$$(T_{q_1} \cdot\cdot T_{q_r}\ T_1^{-1} \cdot T_k^{-1})\,(T_{s_1} \cdot T_{s_\rho})\,(y_n) =$$
$$(T_{q_1} \cdot T_{q_r})\,(T_1^{-1} T_k^{-1}) \cdot (T_{s_1} \cdot T_{s_\rho})\,(y_n) =$$
$$(T_{q_1} T_{q_2} \cdot\cdot T_{q_r} \cdot T_1^{-1} \cdots T_k^{-1} \cdot T_{s_1} \cdot T_{s_\rho})\,(y_n) = S\,(y_n). \qquad [8\cdot20]$$

When B_n converges, then $\sum_{p=0}^{p=\infty} \bar{\beta}_{n,n+p} \leqslant \operatorname{Lt}_{p\to\infty} B_p = K$ for all n. [8·21]

and since $\sum_{p=\infty}^{p=\infty} |d_{n,p}| \leqslant K_1$ and $\sum^{p=\infty} |e_{np}| \leqslant K_2$

$\sum |\gamma_{n,n+p}| \leqslant k\,k_1\,k_2 = k_4$. Let $\bar{y}_A$ be upper bound of $|y_n|$ for $n \geqslant A$;

then $\sum_{p=A}^{\infty} |\gamma_{n,p}\,y_p| \leqslant k_4 \bar{y}_A$. Hence (1) of Theorem VII in this case is proved.

Because of (8·21) (2) of Theorem VII in this case is obvious.

THEOREM VIII: Let $\| \bar{\beta}_{m,n} \| = \| \beta^1{}_{m,n} \| \cdot \| \beta^2{}_{m,n} \| \cdot\cdot\cdot\cdot\cdot \| \beta^k{}_{m,n} \|$ define $(T_1^{-1} T_2^{-1} \cdot T_k^{-1})$.

Let b_ρ be the upper bound of $\bar{\beta}_{n,n+\rho}$ for all n, and $B_n = \sum_{\rho=0}^{n} b_\rho$ as in Theorem VII.

Let T_{ρ_1}, T_{ρ_2}, T_{ρ_r} be r direct T's and $\| d_{m,n} \| = \| a^{\rho_1}{}_{m,n} \| \cdot\cdot\cdot\cdot \| a^{\rho_r}{}_{m,n} \|$ define $(T_{\rho_1} \cdot T_{\rho_2} \cdot T_{\rho_r})$.

Let T_0 and T_0^{-1} be defined by $\| a^0{}_{m,n} \|$ and $\| \beta^0{}_{m,n} \|$.

Let $S = (T_{\rho_1} T_{\rho_2} \cdots T_{\rho_r} T_1^{-1} \cdot\cdot T_k^{-1})$ be defined by $\| d_{m,n} \| \cdot \| \bar{\beta}_{m,n} \| = \| c_{m,n} \|$ and let $S' = (S T_0^{-1})$ be defined by $\| c_{m,n} \| \cdot \| \beta^0{}_{m,n} \| = \| \gamma_{m,n} \|$.

If $y_n = 0\left(\frac{1}{B_n}\right)$ {*i.e.*, $(B_n\,|y_n|)$ is a null sequence}, then

$\{S'\,[T_0\,(y_n)]\} = (S'\,T_0)\,(y_n) = S\,(y_n)$, when the latter exists,

Proof: Let m and p be two any positive integers and $r_{n,n+\mu}$ be

$= \sum_{r=\mu+1}^{\infty} |a^0{}_{n,n+r}|$ as in (5·2).

Let $\bar{y}_{n_0}$ be upper bound of $|y_n|$ for all $n \geqslant n_0$.

Let $T_0\,(y_n) = z_n$.

Then $z_m = \sum_{r=0}^{\infty} a^0{}_{m,m+r}\,y_{m+r} = \sum^{r=\rho} + \sum_{\rho+1}^{\infty} = \sum^{r=\rho} + \theta.\ r_{m,m+\rho}\,\bar{y}_{m+\rho}$

$k \leqslant \rho, \quad z_{m+k} = \sum^{r=\rho} a^0{}_{m+k,m+r}\,y_{m+r} + \theta_k\,r_{m+k,m+\rho}\,\bar{y}_{m+\rho}.$

$$z_{m+\rho} = y_{m+\rho} + \theta_\rho\,r_{n+\rho,n+\rho}\,\bar{y}_{n+\rho}. \qquad [8\cdot22]$$

Consider now

$$\sum_{r=0}^{\rho} \gamma_{m,m+r}\, z_{m+r} = \sum^{r=\rho} \gamma_{m,m+r} \cdot \sum^{s=\rho} a^0_{m+r,m+s}\, y_{m+s} + \bar{y}_{m+\rho} \Sigma\, \theta_r \cdot \gamma_{m,m+r}\, r_{m+r,m+\rho}.$$

$$= \quad A \qquad\qquad + \quad B$$

$$A = \sum^{s=\rho} \left(\Sigma_r\, \gamma_{m,m+r}\, a^0_{m+r,m+s}\right) y_{m+s} = \sum_{s=0}^{s=\rho} c_{m,m+s}\, y_{m+s} \qquad [8\cdot23]$$

$$|B| \leqslant \bar{y}_{m+\rho} \cdot \sum_{r=0}^{\rho} |\gamma_{m,m+r}| \cdot r_{m+r,m+\rho} = \bar{y}_{m+\rho} \cdot B_2 \qquad [8\cdot24]$$

Now $$\gamma_{m,m+r} = c_{m,m+k} \cdot \beta^0_{m+k,m+r}$$

$$\therefore \quad B_2 \leqslant \sum_{r=0}^{\rho} \left(\sum^{k=r} |c_{m,m+k}| \cdot \beta^0_{m+k,m+r} \right) r_{m+r,m+\rho}$$

$$= \sum_{k=0}^{\rho} |c_{m,m+k}| \cdot \sum_{r=k}^{r=\rho} \beta^0_{m+k,m+r}\, r_{m+r,m+\rho}$$

Just as in the course of proof of Theorem IV in (5·4) and (5·5), by (4·6) of Part I

we have $$\sum_{r=0}^{\rho} \beta^0_{m,m+r}\, r_{m+r,m+\rho} \leqslant 1 \quad \text{for all } m \text{ and all } \rho.$$

$$\therefore \quad B_2 \leqslant \sum_{k=0}^{\rho} |c_{m,m+k}| \text{ and } c_{m,m+k} = \sum_{s=0}^{k} d_{m,m+s} \cdot \bar{\beta}_{m+s,m+k}.$$

Hence $$\sum^{k=\rho} |c_{m,m+k}| \leqslant \sum^{k=\rho} \cdot \sum^{s=k} |d_{m,m+s}| \cdot \bar{\beta}_{m+s,m+k}.$$

Now $\bar{\beta}_{m,m+r} \leqslant b_r$. Hence $$\sum^{k=\rho} |c_{m,m+k}| \leqslant \sum^{k=\rho} \cdot \sum^{s=k} |d_{m,m+s}| \cdot b_{k-s}.$$

$$= \sum^{n=\rho} b_n \cdot \sum_{r=0}^{\rho-n} |d_{m,m+r}|.$$

Now by Lemma of (8·1) we have $\sum_{r=0}^{\infty} |d_{m,m+r}| \leqslant K$, a constant.

Hence $B_2 \leqslant K \cdot B_\rho$. [8·25]

Now $|B| \leqslant y_{m+\rho}\, |B_2| \leqslant K \cdot B_\rho \cdot y_{m+\rho} = \dfrac{K \cdot B_\rho \cdot \epsilon_{m+\rho}}{B_{m+\rho}} \leqslant K \cdot \epsilon_{m+\rho}$.

since $y_n = 0\left(\dfrac{1}{B_n}\right)$.

Hence $$\sum^{r=\rho} \gamma_{m,m+r}\, z_{m+r} = \sum^{s=\rho} c_{m,m+s}\, y_{m+s} + \theta K \cdot \epsilon_{m+\rho} \qquad [8\cdot26]$$

If the second series $\sum^{s=\infty} c_{m,m+s}\, y_{m+s}$ converges, then

$$\sum^{r=\infty} \gamma_{m,m+r}\, z_{m+r} = \sum^{s=\infty} c_{m,m+s}\, y_{m+s} \qquad [8\cdot27]$$

i.e., $S'[T_0(y_n)] = (S'\, T_0)(y_n) = S(y_n)$ when the latter exists [8·28]

THEOREM IX : Let S, S′ and T_0 be as in (8·21) and R be $= (T_{q_1}\ T_{q_2} \cdot T_{q_r})$ defined by

$\| e_{m.n} \|$. Then also (S′) $[(T_0\ R)\ (y_n)] = (S'T_0R)\ (y_n)$

$= (SR)\ (y_n)$ if the latter exists

$y_n = 0\left(\frac{1}{B_n}\right)$.

Proof: Let $R\ (y_n) = z_n$ and $\bar{y}_{n_0}$ = upper bound of $|y_n|$ for $n \geqslant n_0$

then $|z_n| = \left| \sum_{p=n}^{\infty} e_{np} y_p \right| \cdot \leqslant \bar{y}_n \cdot \sum_{p=n}^{\infty} |e_{n.p}| \leqslant K\bar{y}_n = 0\left(\frac{1}{B_n}\right)$

Hence $z_n = 0\left(\frac{1}{B_n}\right)$. [8·29]

Now $(T_0\ R)\ (y_n) = T_0\ (z_n)$ and

$S'\ [T_0\ (z_n)] = (S'T_0)\ (z_n) = S\ (z_n)$

$= S\ [R\ (y_n)]$ (if the latter exists). [8·30]

Now the series $\sum_{p=A}^{\infty} |e_{np}|\, y_n| \leqslant \bar{y}_A \cdot K. = 0\left(\frac{1}{B_A}\right)$

since $\sum^{p=\infty} |e_{np}| \leqslant K$ by 8·1.

Hence by Theorem VI $S \cdot R\ (y_n) = (SR)\ (y_n)$ when the latter exists. [8·31]

A particularly interesting case of Theorem IX is when $T_1^{-1} = T_2^{-1} \cdots = T_k^{-1}$ = unit transformation ; then the theorem would be

THEOREM X : If $S = (T_{s_1}\ T_{s_2}\ T_{s_p})$ and y_n a null sequence and $R = (T_{q_1}\ T_{q_2}\ T_{q_r})$

then $(ST_0^{-1})\ [(T_0R)\ (y_n)] = (SR)\ (y_n)$. [8·32]

§ 9. *On Combinations of Inverse* (T^{-1}) *Transformations.*

Most of the theorems in this section are either deductions from, or particular cases of theorems of previous section.

THEOREM XI : Let $R_1 = (T_{q_1} T_{q_2} T_{q_r})$ defined by $\|d_{mn}\| = \|a^{q_1}{}_{m,n}\| \cdots \|a^{q_r}{}_{m,n}\|$

$R_2 = (T_{s_1} \cdot T_{s_2} \cdots T_{s_p})$ ····· $\|e_{m,n}\| = \|a^{s_1}{}_{m,n}\| \cdots \|a^{s_p}{}_{m,n}\|$.

$I = (T_1^{-1}\ T_2^{-1}\ T_k^{-1}) \cdots\cdots$ $\|\bar{\beta}_{m,n}\| = \|\beta^1{}_{m,n}\| \cdots \|\beta^k{}_{m,n}\|$

and $S = (IR_2)$ defined by $\|c_{m,n}\| = \|\bar{\beta}_{m,n}\| \cdot \|e_{m,n}\|$.

If $\sum^{n=\infty} c_{m,n}\, y_n$ converges uniformly for all m, then

$(R_1) \cdot [S\ (y_n)] = (R_1S)\ (y_n)$. [9·1]

This is a particular case of Theorem V and result follows from (8·7).

THEOREM XII : Let $S = (T_1^{-1} T_k^{-1})$ defined by $\| \bar{\beta}_{m,n} \|$.

If $\overset{n=\infty}{\underset{}{\Sigma}} \bar{\beta}_{m,n} y_n$ converges uniformly for all m, then

(1) $(T_l T_{l-1} \cdot T_1)(T_1^{-1} \cdot\cdot T_k^{-1})(y_n) = (T_{l+1}^{-1} \cdots T_k^{-1})(y_n) \quad 0 \leqslant l \leqslant k.$

(2) $(T_k T_{k-1} T_1)(T_1^{-1} \cdot\cdot T_k^{-1})(y_n) = y_n.$

(3) $(T_1^{-1} T_2^{-1} \cdot\cdot T_k^{-1})(y_n) = (T_1^{-1})(T_2^{-1})(T_l^{-1}) \cdot\cdot (T_{l+1}^{-1} \cdots T_k^{-1})(y_n)$
$= (T_1^{-1})(T_2^{-1}) \cdots (T_k^{-1})(y_n).$

Proof:

(1) is a particular case of (8·33) [9·2]

(2) is a particular case of (1) when $l = k$. [9·3]

(3) Let $z_m = \overset{n=\infty}{\underset{}{\Sigma}} \bar{\beta}_{mn} y_n$ then by (1) $(T_l T_{l-1} \cdot T_1)(z_m) =$
$(T_{l+1}^{-1} \cdots T_k^{-1})(y_n) = \alpha_m.$

Since $\Sigma \bar{\beta}_{m,n} y_n$ is uniformly convergent by (3) of theorem V it is a null sequence. By repeated application of Theorem IV of Part I as in corollary to it

$$z_m = \overset{r_1=\infty}{\underset{}{\Sigma}} \beta^1_{m,m+r_1} \cdot \overset{r_2=\infty}{\underset{}{\Sigma}} \beta^2_{m+r,m+r_2} \cdots \overset{\rho=\infty}{\underset{}{\Sigma}} \beta^l_{m+r_{l-1},m+\rho} \cdot \alpha_\rho =$$

$$= (T_1)^{-1} \cdots (T_l)^{-1}(\alpha_m) = (T_1)^{-1}(T_2)^{-1} \cdot (T_l)^{-1}(T_{l+1}^{-1} \cdot\cdot T_k^{-1})(y_n) \quad [9\cdot4]$$

and in particular when $l = k$ $z_m = (T_1)^{-1} \cdot (T_2)^{-1} \cdot\cdot (T_k^{-1})(y_n)$

$$= \overset{r_1=\infty}{\underset{}{\Sigma}} \beta^1_{m,m+r_1} \cdot \overset{r_2=\infty}{\underset{}{\Sigma}} \beta^2_{m+r_1,m+r_2} \cdots \overset{\rho=\infty}{\underset{}{\Sigma}} \beta^k_{m+r_{k-1},m+\rho} y_\rho$$

$$= \overset{\rho=\infty}{\underset{}{\Sigma}} \bar{\beta}_{m,m+\rho} y_\rho \quad [9\cdot5]$$

A particularly interesting case of Theorem VI is the following:

THEOREM XIII : Let $R_1 = (T_{s_1} \cdot T_{s_2} \cdot T_{s_3} \cdot T_{s_p})$, be defined by $\| d_{mn} \|$
and $R_2 = (T_1^{-1} \cdot\cdot T_k^{-1})$ $\| \bar{\beta}_{m\,n} \|$.

and $S = (T_{\rho_1}^{-1} \cdots T_{\rho_l}^{-1} T_{q_1} T_{q_2} \cdots T_{q_r})$ defined by $\| c_{m,n} \|$.

If $\left| \overset{\infty}{\underset{n=A}{\Sigma}} c_{m,n} y_n \right| = 0\left(\frac{1}{B_A}\right)$ for all m

then $(R_1 R_2)\,[S(y_n)]\,(R_1 R_2 S)(y_n)$ when the latter exists. [9·6]

THEOREM XIV : Let $(T_1^{-1} T_2^{-1} \cdot T_k^{-1})$ be defined by $\| \bar{\beta}_{m,n} \|$ then if $\Sigma \bar{\beta}_{mn} \| y_n \|$ converges for all m, then the terms of the product $(T_1^{-1} \cdot T_k^{-1})$ can be associated in any arbitrary manner, and the resultant of all the associations on y_n is equal to $(T_1^{-1} T_2^{-1} T_k^{-1})(y_n)$.

We shall take a particular association and prove it, the proof for all other associations being the same.

Let $(T_1^{-1} \cdot T_2^{-1} \cdot T_{l_1}^{-1})$ be defined by $\| \bar{\beta}'_{m,n} \|$.

$(T_{l_1+1}^{-1} \cdots T_{l_2}^{-1})$ $\cdots$ $\| \bar{\beta}''_{m,n} \|$

$(T_{l_2+1}^{-1} \quad T_k^{-1})$ $\cdots$ $\| \bar{\beta}'''_{m,n} \|$.

To prove $\sum_{n_1=\infty}^{n_1=\infty} \bar{\beta}'_{m,n_1} \cdot \sum_{n_2=\infty}^{n_2=\infty} \bar{\beta}''_{n_1,n_2} \cdot \sum_{p=\infty}^{p=\infty} \bar{\beta}'''_{n_2,p}\, y_p = \sum_{p=\infty}^{p=\infty} \bar{\beta}_{m,p}\, y_p$.

Now all the $\beta_{m,n} \geqslant 0$, and $\| \bar{\beta}'_{m,n} \| \cdot \| \bar{\beta}''_{m,n} \| \cdot \| \bar{\beta}'''_{m,n} \| = \| \bar{\beta}_{m,n} \|$

Since $\Sigma\, \bar{\beta}_{mp} \mid y_p \mid$ converges

$$\sum_{\rho=\infty}^{\rho=\infty} \bar{\beta}_{m\rho}\, y_\rho = \sum_{p=\infty}^{p=\infty} (\Sigma\Sigma\, \bar{\beta}'_{mp_1} \cdot \bar{\beta}''_{p_1,p_2} \cdot \bar{\beta}'''_{p_2,p})\, y_p.$$

$$= \sum_{p_1=\infty}^{p_1=\infty} \bar{\beta}'_{m,p_1} \cdot \sum_{p_2=\infty}^{p_2=\infty} \bar{\beta}''_{p_1,p_2} \sum_{p=\infty}^{p=\infty} \bar{\beta}'''_{p_2,p}\, y_p$$

i.e., $(T_1^{-1} T_2^{-1} T_{l_1}^{-1})\,(T_{l_1+1}^{-1} \cdots T_{l_2}^{-1})\,(T_{l_2+1}^{-1} \cdot T_k^{-1})\,(y_n)$

$= (T_1^{-1} \cdots T_k^{-1})\,(y_n)$. [9·7]

THEOREM XV : $\| \bar{\beta}_{m,n} \|$ defines $(T_1^{-1} \cdots T_k^{-1})$. If $\Sigma\, \bar{\beta}_{m,n} \mid y_n \mid$ converges uniformly for all m then (1), (2), (3) of Theorem XII and the conclusion of XIV are all true in this case.

This is obvious. An interesting case of this is when $y_n = 0\left(\frac{1}{B_n^{1+\delta}}\right)$ for by Theorem VII $\Sigma\, \bar{\beta}_{m,n} \mid y_n \mid$ converges uniformly if $y_n = 0\left(\frac{1}{B_n^{1+\delta}}\right)$. [9·8]

§ 10. *On the Properties of a Particular Subclass of* (T).

We notice that in the theorems proved till now, in order that a combination of inverse and direct transformations on a sequence $\{y_n\}$ may be valid, there must be some strict restriction on y_n (for *e.g.*, in Theorem IV, $y_n \to 0$ as $n \to \infty$). In general, when a combination involves an inverse, the restriction on y_n is greater than when the combination is purely of direct T's in which latter case the only restriction being y_n be bounded. In § 10 we deal with a subclass of (T) designated by $\bar{T}_0$. The algebra of combinations involving any number of T's and $(\bar{T})^{-1}$ is very simple and exactly like that of direct (T) transformation combinations.

The matrix $\| \bar{a}_{m,n} \|$ of a $\bar{T}$ is characterised by the following :

($\bar{a}$) $\bar{a}_{nn} = 1$ ($\bar{b}$) $\bar{a}_{m,n} = 0$, $n < m$ ($\bar{c}$) $a_{m,n} \leqslant 0$, $n > m$ and

($\bar{d}$) $-\sum_{\rho=1}^{\infty} \bar{a}_{m,m+\rho} \leqslant k < 1$ for all m ; where the first three conditions are the same as in (2·1) for a T and ($\bar{d}$) is a greater restriction than (d) of (2·1) [10·1]

From (4·7) if $\| \bar{\beta}_{mn} \|$ defines a $(\overline{\mathrm{T}})^{-1}$ then $\sum_{\rho=0}^{\infty} \bar{\beta}_{m,\,m+\rho} \leqslant \frac{1}{1-k}$. [10·2]

Let us designate the matrix of any T, $\overline{\mathrm{T}}$ or $(\overline{\mathrm{T}})^{-1}$ by $\| b_{mn} \|$. Then from (10·1), and (10·2) and condition (*d*) of (2·1) we have $\sum_{\rho=0}^{\infty} | b_{m,\,m+\rho} | \leqslant \mathrm{K}$ (a constant) for all m. [10·3]

If V stands for any T, $\overline{\mathrm{T}}$, or $(\overline{\mathrm{T}})^{-1}$ the most general theorem involving T, $\overline{\mathrm{T}}$ and $(\overline{\mathrm{T}})^{-1}$ will be the following :

THEOREM XVI: If $\{x_n\}$ be $\left\{\frac{\text{bounded}}{\text{null}}\right\}$ sequence so is $(\mathrm{V}_1, \mathrm{V}_2 \cdot\cdot \mathrm{V}_k)\ (x_n)$, and $(\mathrm{V}_1\, \mathrm{V}_2\, \mathrm{V}_k)\ (x_n) = (\mathrm{V}_1\, \mathrm{V}_2 \cdot\cdot \mathrm{V}_\rho) \cdot\cdot (\mathrm{V}_{\rho+1} \cdot\cdot \mathrm{V}_l) \cdot\cdot (\mathrm{V}_{l+1} \cdot \mathrm{V}_k)\ (x_n)$. Proof is immediate because it means that all $(\overline{\mathrm{T}})^{-1}$ behave exactly like the direct transformation T. [10·4]

In particular it is interesting to notice the form which Theorem IV and its complement take in the case of $\overline{\mathrm{T}}$ and T^{-1}.

THEOREM XVII : $\{x_n\}$ being a bounded sequence, if $\overline{\mathrm{T}}\ (x_n) = y_n$, then

(1) $x_n = (\overline{\mathrm{T}})^{-1}\ (y_n)$;

(2) Given $\{y_n\}$ the infinite set of equations $\mathrm{T}\ (x_n) = \Sigma\ \bar{a}_{m,\rho}\ x_\rho = y_m$, $m = 0, 1, 2, \cdots n$,—under the restriction x_n be bounded, has utmost one solution.

(3) The necessary and sufficient condition that the infinite set of equations $\Sigma\ \bar{a}_{m,\,\rho}\, x_\rho = y_m$ has one solution $\{x_n\}$ under the restriction that x_n be bounded is that y_n be bounded.

The proofs of (1), (2) and (3) follow very simply from Theorem XI. [10·5]

§ 11. *Two theorems applicable for a special subclass of* (*T*).

Let T_0 be defined by $\| a^0_{m,\,n} \|$ and T_0^{-1} by $\| \beta^0_{m,\,n} \|$.

Let S be any transformation denoted by $\| s_{m,\,n} \|$ where $s_{m,\,n} = 0$, $n < m$;

THEOREM XVIII : If (1) $\{x_n\}$ be a bounded sequence and (2) $\frac{s_{m,\,m+p}}{\mathrm{B}^0_{m,\,m+p}} \to 0$ as $p \to \infty$ for every m and (3) $| s_{m,\,n} | \leqslant \mathrm{K}'$ for all m, n,

then $\mathrm{S}\ [\mathrm{T}_0\ (x_n)] = (\mathrm{S}\ \mathrm{T}_0)\ (x_n)$, when the latter exists.

Proof :

Let $|x_n| < \mathrm{K}$. Let $\sum_{\rho=p+1}^{\infty} |a^0_{n,\,n+\rho}| = -\sum_{\rho=p+1}^{\infty} a^0_{n,\,n+\rho} = r_{n,\,n+p}$, $p \geqslant 1$ and let $\mathrm{T}_0\ (x_n) = y_n$.

Then $y_n = \sum_{\rho=0}^{\infty} a^0_{n,\,n+\rho}\, x_{n+\rho} = \sum_{\rho=0}^{p} + \sum_{p+1}^{\infty} = \sum^{\rho=p} + \theta \mathrm{K} \cdot r_{n,\,n+p}.$

Similarly $y_{n+k} = \sum^{\rho=p} a^0_{n+k,\,n+\rho}\, x_{n+\rho} + \theta_k \cdot \mathrm{K} \cdot r_{n+k,\,n+p}$ [11·1]

for $k = 0, 1, 2, p.$ and $-1 \leqslant \theta_k \leqslant 1.$

Then $\sum_{\rho=0}^{\rho=p} s_{n,\,n+\rho}\, y_{n+\rho} = \sum^{\rho=p} s_{n,\,n+\rho} \cdot \sum^{\rho'=p} a^0_{n+\rho,\,n+\rho'}\, x_{n+\rho'} +$

$$\mathrm{K} \Sigma\, \theta_\rho\, s_{n,\,n+\rho} \cdot r_{n+\rho,\,n+\rho}$$

$$= \mathrm{A} + \mathrm{B}. \qquad [11\cdot2]$$

$$\mathrm{A} = \sum_{\rho'=0}^{\rho'=p} \Big(\sum_{\rho=0}^{\rho=\rho'} s_{n,\,n+\rho} \cdot a^0_{n+\rho,\,n+\rho'} \Big) \cdot x_{n+\rho'}$$

$$|\mathrm{B}| \leqslant \mathrm{K} \cdot \sum_{\rho=0}^{p} |s_{n,\,n+\rho}|\, r_{n+\rho,\,n+p} = \mathrm{K} \Big(\sum^{k-1} + \sum_{k}^{p} \Big) = \mathrm{K}\,(\beta_1 + \beta_2);$$

choose k sufficiently large such that for $\rho \geqslant k$, $\dfrac{|s_{n,\,n+\rho}|}{\beta^0_{n,\,n+\rho}} \leqslant \epsilon$

$$\mathrm{B}_2 \leqslant \epsilon \cdot \sum_{\rho=k}^{\rho=p} \beta^0_{n,\,n+\rho} \cdot r_{n+\rho,\,n+p} \leqslant \epsilon \cdot \sum_{\rho=0}^{\rho=p} \beta^0_{n,\,n+\rho} \cdot r_{n+\rho,\,n+p}.$$

Now $r_{n,\,n+p} = \sum_{p+1}^{\infty} - a^0_{n,\,n+\rho} = \sum_{\rho=1}^{\infty} - \sum^{\rho=p} \leqslant \mathrm{R}_{n,\,n+p}$ of (4.6 *a*)

and by (4·6 *a*) $\Sigma\, \beta^0_{n,\,n+\rho}\, \mathrm{R}_{n+\rho,\,n+p} = 1$; Hence $\mathrm{B}_2 \leqslant \epsilon.$ [11·3]

Now $\mathrm{B}_1 \leqslant \mathrm{K}' \sum_{\rho=0}^{\rho=k-1} r_{n+\rho,\,n+p}$ by hypothesis (3).

Now each of the sequences $r_{n,\,n+p},\ r_{n+1,\,n+p} \cdots r_{n+k-1,\,n+p}$ tends to zero by condition (*d*) of 2·1; choosing p sufficiently large, $\mathrm{B}_1 \leqslant \epsilon.$

Hence for sufficiently large p $|\mathrm{B}| \leqslant \epsilon\ (\rho)$ and we have [11·4]

$$\sum_{\rho=0}^{\rho=p} s_{n,\,n+p} \cdot y_{n+\rho} = \sum_{\rho=0}^{\rho=p} \Big(\Sigma_{\rho_1}\, s_{n,\,n+\rho_1}\, a^0_{n+\rho_1,\,n+\rho} \Big)\, x_{n+\rho} + \theta\epsilon\ (p).$$

$$= \sum_{\rho=0}^{p} d_{n,\,n+\rho}\, x_{n+\rho} + \theta\epsilon\ (p) \qquad [11\cdot5]$$

where $\| d_{m,\,n} \| = \| s_{m,\,n} \| \cdot \| a^0_{m,\,n} \|.$

If the latter series $\sum^{p=\infty} d_{n\,p}\, x_p$ converges then in the limit making $p \to \infty$

$$\sum^{\rho=\infty} s_{n,\,n+\rho}\, y_{n+\rho} = \sum_{\rho=0}^{\infty} d_{n,\,n+\rho}\, x_{n+\rho} \quad \text{or}$$

$$\mathrm{S}\,[\mathrm{T}_0\,(x_n)] = (\mathrm{S}\,\mathrm{T}_0)\,(x_n) \text{ when the latter exists.} \qquad [11\cdot6]$$

THEOREM XIX. Let T_1 and T_2 and (T_1T_2) be defined by $\| a_{m,n} \|$, $\| b_{m,n} \|$ and $\| c_{mn} \| = \| a_{m,n} \| \cdot \| b_{m,n} \|$.

Let (1) $\sum_{\rho=p+1}^{\infty} |a_{m,m+p}| = r^a_{m,m+p}$

(2) $\sum_{\rho=p+1}^{\infty} |c_{m,m+p}| = r^c_{m,m+p}$

and T_1^{-1} be defined by $\| \beta_{m,n} \|$.

Then if (1) $\frac{r^c_{m,m+p}}{r^a_{m,m+p}} \to 0$ as $p \to 0$ uniformly for all m (2) $\beta_{n,n+p} \to 0$ as $p \to \infty$.

and (3) $|x_n| \leqslant K$, then

$$(T_1^{-1} \cdot)\,[(T_1T_2)\,(x_n)] = T_2\,(x_n). \qquad [11\cdot 7]$$

Proof: Let $(T_1T_2)\,(x_n) = y_n$ and p a positive integer

and $y_n = \sum_{\rho=0}^{\rho=\infty} c_{n,n+\rho}\, x_{n+\rho} = \sum_{\rho=0}^{\rho=p} + \sum_{p+1}^{\infty} = \sum_{\rho=0}^{\rho=p} + K.\theta\, r^c_{n,n+p}$

Similarly $y_{n+k} = \sum_{\rho=0}^{\rho=p} c_{n+k,n+\rho}\, x_{n+\rho} + K.\,\theta_k.\, r^c_{n+k,n+p}$ $[11\cdot 8]$

for $k = 0, 1, p$ and $-1 \leqslant \theta_k \leqslant 1$.

$$\sum_{\rho=0}^{\rho=p} \beta_{n,n+\rho}\, y_{n+\rho} = \sum_{\rho=0}^{\rho=p} \beta_{n,n+\rho} \cdot \sum_{s=0}^{s=p} c_{n+\rho,n+s}\, x_{n+s} + K \Sigma\, \theta_\rho \cdot \beta_{n,n+\rho} \cdot r^c_{n+\rho,n+p}$$

$$= A + B.$$

$$A = \sum_{s=0}^{p} \cdot \Big(\sum_{\rho=0}^{s} \beta_{n,n+\rho}\, c_{n+\rho,n+s}\Big) \cdot x_{n+s} = \sum_{s=0}^{s=p} b_{n,n+s}\, x_{n+s}$$

$$|B| \leqslant K \cdot \Big(\sum_{\rho=0}^{p-k} \beta_{n,n+\rho}\, r^c_{n+\rho,\,n+p} + \sum_{p-k+1}^{p}\Big) = K\,(B_1 + B_2) \qquad [11\cdot 9]$$

Choosing k large enough such that $\frac{r^c_{n,n+\rho}}{r^a_{n,n+\rho}} \leqslant \epsilon$ for all n and $\rho \geqslant k$

$$B_1 \leqslant \epsilon \cdot \sum_{\rho=0}^{\rho=p-k} \beta_{n,n+\rho}\, r^a_{n+\rho,n+p}$$

$$\leqslant \epsilon \cdot \sum_{\rho=0}^{\rho=p} \beta_{n,n+\rho} \cdot r^a_{n+\rho,n+p} \leqslant \epsilon \quad \text{just as in } (12\cdot 3). \qquad [11\cdot 10]$$

and $B_2 = \sum_{\rho=p-k+1}^{\rho=p} \beta_{n,n+\rho}\, r^c_{n+\rho,\,n+p} \leqslant K_1 \sum_{\rho=p-k+1}^{\rho=p} \beta_{n,n+\rho}$

since by condition (d) of $(2\cdot 1)$ for T_1 and T_2, $r^c_{n,p} \leqslant K_1$ for all n and p.

Choosing p sufficiently large, by condition (2) of Theorem XIX, we have

$$\sum_{\rho=p-k+1}^{\rho=p} \beta_{n,n+\rho} \leqslant \epsilon, \text{ i.e., } B_2 \leqslant \epsilon' (p)$$

Hence
$$| B | \leqslant \epsilon'' (\rho) \qquad [11\cdot11]$$

and
$$\sum^{\rho=p} \beta_{n,n+\rho}\, y_{n+\rho} = \sum^{\rho=p} b_{n,n+\rho}\, x_{n+\rho} + \theta\epsilon'' (p)$$

and in the limit
$$\sum^{\rho=\infty} \beta_{n,n+\rho}\, y_{n+\rho} = \sum^{\rho=\infty} b_{n,n+\rho}\, x_{n+\rho} \quad \text{or}$$
$$(T_1^{-1})\,[(T_1T_2)\,(x_n)] = T_2\,(x_n). \qquad [11\cdot12]$$

§ 12. *On an Integral Equation.*

Corresponding to a T for a sequence, we define the following transformation for the continuous variable.

Let (1) $K(x, t) \geqslant 0$ for all $x \geqslant 0$, $t \geqslant 0$; (2) $K(x, t) = 0$, $t < x$;
(3) $K(x, t)$ being continuous in (x, t), for all $x \geqslant 0$, $t \geqslant 0$.

$$(4)\ \int_0^\infty K(x, t)\, dt \leqslant 1 \text{ for all } x. \qquad [12\cdot1]$$

Let $u(t)$ be a given continuous function defined for $t \geqslant 0$, then the transformation T will be $T(u) = u(t) - \int_0^\infty K(t, r)\, u(r)\, dr = v(t)$. $\qquad [12\cdot2]$

We discuss here only the existence of the inverse of this transform and show that under certain conditions $u(t) = T^{-1}\{v(t)\}$. The main point of interest in the solution of the integral equation in u of (12·2) is that the range is infinite. We shall show that the solution can be given in terms of Volterra's reciprocal of $K(x, t)$ just as in the ordinary case of finite range when $v(t)$ satisfies a certain condition.

THEOREM XX: (1) If $u(x) \to 0$ as $x \to \infty$ and

$$T(u) = u(x) - \int_0^\infty K(x, t)\, u(t)\, dt = v(x),$$

then
$$u = T^{-1}[(v(x)] = v(x) + \int_0^\infty \overline{K}(x, t).\, v(t)\, dt.$$

where
$$[\overline{K}(x, t)] = K(x, t) + K_1(x, t) + \cdots K_n(x, t) + \cdots$$

where
$$[\overline{K}_n(x, t)] = \int_0^t K_{n-1}(x, u)\, K(u, t)\, dt.$$

(2) Given $v(x)$, the equation $T(u) = v$ will have utmost one solution under the restriction $u(x) \to 0$ as $x \to \infty$.

(3) Given $v(x)$ the necessary and sufficient condition that the equation $T(u) = v$ has one solution under the restriction $u(x) \to 0$ as $x \to \infty$ is that

$$\int_0^\infty \overline{K}(x, t)\, v(t)\, dt \text{ converges uniformly for all } x \geqslant 0.$$

Lemmas:

(1) $K_n(x, t) = 0 \quad t < x$ (proof by mathematical induction and (2) of (12·1)) [12·3]

(2) $K_n(x, t) \geqslant 0$ for x and t, obvious from definition. [12·4]

(3) By definition $K_n(x, t) = \int_0^t K_{n-1}(x, u).\ K(u, t)\, du$. To prove

$$K_n(x, t) = \int_0^t K_{n-1}(u, t).\ K(x, u)\, du, \qquad [12\cdot5]$$

suppose this is true for $1, 2, \cdots n-1$, then we will prove it is true for n and hence for all $n \geqslant 1$ since it is true for $n \geqslant 1$.

By definition $K_n(x, t) = \int_0^t K(u, t) \cdot K_{n-1}(x, u)\, du$

and by hypothesis $K_{n-1}(xu) = \int_0^t K_{n-2}(u, t) \cdot K(xu)\, du$.

Hence $K_n(x, t) = \int_0^t K(u, t) \cdot du \cdot \int_0^u K(xv) \cdot K_{n-2}(v, u)\, dv$

$$= \int_0^t K(x, v)\, dv \int_v^t K(u, t)\, K_{n-2}(vu)\, du$$

$$= \int_0^t K(x, v)\, dv \int_0^t K(u, t)\, K_{n-2}(v, u)\, du$$

since $K_n(v, u) = 0$ $u < v$

$$= \int_0^t K(x, v)\, K_{n-1}(vt)\, dt \qquad [12\cdot5]$$

for $n = 1$. (12·5) is obvious since $K_n(x, t) \equiv K(x, t)$. Hence (12·5) is true for $n \geqslant 1$.

(4) $\sum_0^\infty K_n(n, t)$ converges. This follows from continuity of $K(x, t)$ in $x \geqslant 0, t \geqslant 0$ [12·6]

(5) $\overline{K}(x, t)$ is continuous; this follows from uniform convergence of ΣK_n and continuity of K_n. [12·7]

(6) (1) $\overline{\mathrm{K}}(x, t) \geqslant 0$ for all x, t; (2) $\overline{\mathrm{K}}(x, t) = 0 \quad t < x$. (1) is obvious, (2) follows from (12·3).

(7) The reciprocal function $\overline{\mathrm{K}}(x, t)$ satisfies two integral equations.

$$\mathrm{K}(x, t) - \mathrm{K}(x, t) = \int_0^t \mathrm{K}(x, u)\,\mathrm{K}(u, t)\,dt = \int_0^t \overline{\mathrm{K}}(u, t)\cdot\mathrm{K}(x, u)\,du.$$

This follows immediately from definition of K_n and (12·5), and term by term integration of $\Sigma\,\mathrm{K}_n(x)$. [12·8]

(8) Let $\mathrm{R}(x, \mathrm{A}) = 1 - \int_0^{\mathrm{A}} \mathrm{K}(x, t)\,dt$. To prove

$$\int_0^{\mathrm{A}} \overline{\mathrm{K}}(x, u)\cdot\mathrm{R}(u, \mathrm{A})\,du = 1 - \mathrm{R}(x, \mathrm{A}). \qquad [12\cdot9]$$

Proof: $\int_0^{\mathrm{A}} \overline{\mathrm{K}}(x, u)\left\{1 - \int_0^{\mathrm{A}} \mathrm{K}(u, t)\,dt\right\} du = \int_0^{\mathrm{A}} \overline{\mathrm{K}}(x, u)\,du$

$$- \int_0^{\mathrm{A}} \overline{\mathrm{K}}(x, u)\left\{\cdot\int_0^{\mathrm{A}} \mathrm{K}(u, b)\,dt\right\} du = \alpha - \beta.$$

$\beta = \int_0^{\mathrm{A}} \overline{\mathrm{K}}(x, u)\,du \int_u^{\mathrm{A}} \mathrm{K}(u, t)\,dt$, since $\mathrm{K}(u, t) = 0 \quad t < u$

$= \int_0^{\mathrm{A}} dt\cdot\int_0^t \overline{\mathrm{K}}(x, u)\,\mathrm{K}(u, t)\,du = \int_0^{\mathrm{A}} \{\overline{\mathrm{K}}(x, t) - \mathrm{K}(x, t)\}\,dt$ by (12·8)

Hence $\alpha - \beta = \int_0^{\mathrm{A}} \mathrm{K}(x, t)\,dt = 1 - \mathrm{R}(x, \mathrm{A})$

$$= \int_0^{\mathrm{A}} \overline{\mathrm{K}}(x, u)\,\mathrm{R}(u, \mathrm{A}) \qquad [12\cdot9]$$

(12·9) corresponds to formula (4·7) in Part I.

Proof (1) of Theorem XX:—

$$\int_0^{\mathrm{A}} \overline{\mathrm{K}}(xt)\,v(t)\,dt = \int_0^{\mathrm{A}} \overline{\mathrm{K}}(x, t)\,u(t)\,dt - \int_0^{\mathrm{A}} \overline{\mathrm{K}}(x, t)\,dt \int_0^{\infty} \overline{\mathrm{K}}(t, z)\,u(z)\,dz \text{ by } (12\cdot2)$$

$$= \mathrm{B}_1 - \mathrm{B}_2. \qquad [12\cdot10]$$

Let $\bar{u}(z_0)$ be the upper bound of $|u(z)|$ for $z \geqslant z_0$

then $\int_0^{\infty} \overline{\mathrm{K}}(tz)\,u(z)\,dz = \int_0^{\mathrm{A}} + \int_{\mathrm{A}}^{\infty} = \int_0^{\mathrm{A}} + \theta\cdot r(t, \mathrm{A})\cdot\bar{u}(\mathrm{A}_0), \qquad [12\cdot11]$

where $r(t, \mathrm{A}) = \int_{\mathrm{A}}^{\infty} \mathrm{K}(tz)\,dz$ and $-1 \leqslant \theta \leqslant 1$.

$$\text{Hence } B_2 = \int_0^A \bar{K}(x,t)\,dt \int_0^A K(tz)\,dz + \bar{u}\cdot(A)\cdot\int_0^A \theta\cdot\bar{K}(x,t)\cdot r(t,A)\,dt$$
$$= C_1 + C_2. \qquad [12\cdot12)$$

$$\text{Now } r(t,A) = \int_0^\infty K(t,z)\,dz - \int_0^A K(tz)\,dz \leqslant 1 - \int_0^A = R(t,A).$$

$$\text{Hence } |c_2| \leqslant \bar{u}(A)\cdot\int_0^A \bar{K}(x,t)\cdot R(t,A)\,dt = \bar{u}(A)\{1 - R(x,A)\} \text{ by } (12\cdot9)$$

$$\text{and } c_1 = \int_0^A \bar{K}(x,t)\,dt \int_t^Z K(tz)\cdot u(z)\,dz \text{ since } K(tz) = 0,\quad z < t$$
$$= \int_0^A u(z)\,dz\cdot\int_0^Z \bar{K}(x,t)\,K(t,z)\,dt$$
$$= \int_0^A (\bar{K}(x,z) - K(x,z)\cdot u(z)\,dz. \qquad [12\cdot13]$$

$$\text{Hence } B_1 - B_2 = \int_0^A K(x,z)\,u(z) + \theta' u(A)\{1 - R(x,A)\} \qquad [12\cdot14]$$
$$= \int_0^\infty K(x,z)\,\bar{u}(z) + \theta''\,R(x,A)\,u(A) + \theta'\cdot\{1 - R(x,A)\}\,\bar{u}(A)$$
$$= \int_0^\infty \bar{K}(x,z)\,u(z)\,dz + \theta'''\,\bar{u}(A) \qquad [12\cdot15]$$

$$\text{Hence } \int_0^A \bar{K}(xt)\,v(t)\,dt = \int_0^\infty K(x,z)\,u(z)\,dz + \theta'''\,\bar{u}(A)$$
$$= u(x) - v(x) + \theta'''\,\bar{u}(A). \qquad [12\cdot16]$$

Since $\bar{u}(A) \to 0$, $A \to \infty$ by hypothesis, we have

$$u(x) = v(x) + \int_0^\infty K(x,t)\,v(t)\,dt = T^{-1}\{v(x)\}. \qquad [12\cdot17]$$

Proofs of (2) and (3) of Theorem XX follow almost exactly by the same way as the corresponding portion of the Theorem IV of Part I and complement of Theorem IV of Part I.

MAGNETIC ANISOTROPY AND PLEOCHROISM OF BIOTITE MICA.

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1. *Introduction.*

The micas constitute a highly interesting class of minerals on account of their characteristic crystalline structure and optical properties. Most varieties contain iron to a greater or less extent, in the combined state as well as in the form of inclusions, and as a result they are generally paramagnetic.[1] Biotite is distinguished by the presence in it of comparatively large amounts of iron, and its characteristic optical property is a strong pleochroism in the visible region of light. Light vibrations parallel to the cleavage plane are strongly absorbed, whereas vibrations normal to the plane are more or less freely transmitted. It is also well known that pleochroism is most marked in varieties rich in iron. The present investigation was undertaken in the hope that a study of the paramagnetic anisotropy, susceptibility and pleochroism of biotites of known composition might lead to interesting results regarding the nature and origin of these properties, while serving to throw light on the probable connection between pleochroism and magnetic anisotropy in paramagnetic solids.

The magnetic anisotropy of a large number of varieties of mica has been studied by E. Wilson.[2] He examined both spotted as well as clear varieties and in all cases found that the paramagnetic susceptibility parallel to the cleavage plane was much greater than that perpendicular to it. The ratio $\frac{\chi_{\parallel}}{\chi_{\perp}}$ was very much greater in the spotted varieties. It was not clearly stated to which group the specimens belonged. Presumably only muscovite was examined. It was tentatively suggested that the anisotropy might be due to either an orderly arrangement of the inclusions of magnetite present, or an actual difference in the behaviour of the mica itself in different directions relative to the crystallographic axes. No attempt was made, however, to decide between the two hypotheses. The position has now altered considerably. Clear inclusion-free specimens of mica containing iron which forms an integral part of the lattice (as in pholgopite and biotite) may well show a

genuine crystalline magnetic anisotropy. In the light of the X-ray crystallographic data now available[3] and recent developments in the theory of the magnetic anisotropy of paramagnetic solids due to Van Vleck and Penney and Schlapp,[4] a satisfactory interpretation of the magnetic data is now possible. In the present investigation the author has determined the susceptibility and magnetic anisotropy of three varieties of biotite and one each of muscovite and phlogopite. The ferrous and ferric iron contents of the specimens were determined by chemical analysis and the pleochroism of the specimens also estimated quantitatively.

2. Crystal Structure and Chemical Constitution of the Micas.

According to the recent theory developed by Van Vleck and Penney and Schlapp, the asymmetry of the strong crystalline electric fields acting on the paramagnetic ion is primarily responsible for magnetic anisotropy in paramagnetic solids. These electric fields are due to the environment of anions or dipole molecules which are grouped around the cation. The symmetry and nature of the grouping determines the character of the crystal fields and hence the magnetic anisotropy, in the case of any particular paramagnetic ion. A knowledge of the exact disposition of the atoms in the crystal lattice is thus necessary for the interpretation of the magnetic data in the light of theory.

The general scheme of the atomic structure of the micas was first elucidated by Pauling[5] and the full investigation in the case of muscovite has been made by Jackson and West.[6] It has been shown that all the micas are built more or less according to the same plan. The peculiar flaky structure and easy cleavage have been explained as being due to the formation of sheets of linked silicon-oxygen tetrahedra. A sheet is formed by linking the oxygen atoms at the corners of the tetrahedra so that they are all in the same plane and the result is a hexagonal network. Two such sheets placed with the vertices of the tetrahedra pointing inwards form a double sheet, the oxygen atoms at the vertices being cross-linked by aluminium atoms in muscovite, and magnesium and iron atoms in phlogopite and biotite. Hydroxyl groups are incorporated, linked to Al, Mg or Fe alone. We have thus a firmly bound double-sheet and the mica structure is a succession of such double-sheets interspaced alternately by sheets of potassium atoms. The iron atoms occupy positions of six co-ordination and are surrounded by an octahedral grouping of oxygen atoms and hydroxyl groups. X-ray evidence has shown that such a grouping is present in the hydrated sulphates and double-sulphates of iron, cobalt, nickel, etc., the water molecules in these salts constituting the octahedral environment. The crystalline electric

fields due to such an arrangement are presumably of a highly asymmetric character as has been pointed out by Krishnan recently.

The chemical composition of the micas is variable within wide limits. Since the magnetic properties are determined by the iron content, as will be seen later, it is essential to know accurately the amount of iron present. In fact many properties of mica show a direct dependence on chemical composition. Kunitz[7] has made a detailed study, combining optical and density determinations with chemical analysis. He established three series of isomorphous replacements and showed that the change in optical properties within one series depended mainly on the iron content. Similar classifications have been made by Hallimond, Winchell and Jakobs, and recently Niggli[8] while discussing a recent paper by J. Holzner on the crystal structure of biotite, has summarised the evidence from reliable chemical analysis and has pointed out the variability of the three types, *i.e.*, the muscovite type, the lithia mica type and the phlogopite-biotite type. A consideration of the physical properties in relation to chemical constitution shows that we cannot speak of a continuous transition from one group to another. This is probably due to the fact that the properties depend on the structure also besides chemical composition, and differences among the three types exist although the general plan of their architecture is similar. G. Nagelschmidt[9] has recently found from an examination of the X-ray powder diagrams of eight different micas of known composition, density and optical properties, that they belong to at least two distinct types, the muscovite type and the phlogopite-biotite type. The lithia mica type could not, however, be distinguished.

The principles governing isomorphous substitution in the micas were established by the work of Mauguin[10] who measured the dimensions of the unit cell in varieties of known density and composition. Ideal formulæ have been assigned based on such measurements, as follows:

Muscovite	..	$K\,Al_2\,(AlSi_3O_{10})\,(OH)_2$
Phlogopite	..	$K\,Mg_3\,(AlSi_3O_{10})\,(OH)_2$
Biotite	..	$K\,(Mg, Fe)_3\,(AlSi_3O_{10})\,(OH)_2$

3. *Determination of Magnetic Anisotropy.*

The magnetic anisotropy has been measured by the torsional method developed by Krishnan.[11] If an anisotropic crystal is suspended with one of its axes vertical by means of a fine quartz fibre in a uniform magnetic field, the forces acting upon it will be (1) a couple due to anisotropy of shape which will tend to rotate the crystal such that its length is along the field and (2) couple due to the magnetic anisotropy which will tend to rotate the crystal such that the direction of algebraically maximum susceptibility in the

horizontal plane is parallel to the field. Let us assume that (1) is negligible compared with (2). Let $\chi_{max.}$ and $\chi_{min.}$ be the maximum and minimum susceptibilities in the plane. If initially the torsion head of the fibre is adjusted that $\chi_{max.}$ is parallel to the field direction no couple acts on the crystal when the field is put on. If now the torsion head is turned round, the crystal also turns round but to a smaller extent on account of the couple due to magnetic anisotropy which begins to act on it when it leaves the zero position. At a critical position when $\chi_{max.}$ and $\chi_{min.}$ are making 45° with the field direction, this couple is a maximum and with the smallest further rotation of the torsion head the crystal will quickly turn round. If α_c is the angle through which the torsion head has been turned round, the specific anisotropy in the plane is given by the relation.

$$\chi_{max.} - \chi_{min.} = 2\left(\alpha_c - \frac{\pi}{4}\right)\frac{c}{m\,H^2}$$

where c is the torsional constant of the fibre, H the field strength and m the mass of the crystal. The micas crystallise on the monoclinic system and there are three principal susceptibilities of which two lie in the symmetry plane and the third along the symmetry axis. We have to determine the quantities $(\chi_1 - \chi_2)$, $(\chi_1 - \chi_3)$ and the relative orientation of the axes of the magnetic ellipsoid with respect to the crystallographic axes. χ_1 and χ_2 are the principal susceptibilities in the b (010) plane, χ_2 being nearer the a-axis and χ_3 is the principal susceptibility in the direction of the b-axis. The mica specimen was suspended in the uniform magnetic field as follows :— (1) with the cleavage plane horizontal, (2) with the b-axis vertical and (3) with the b-axis horizontal and the cleavage plane vertical. We thus directly determine the quantities $(\chi_3 - \chi_a)$, $(\chi_1 - \chi_2)$ and $(\chi_3 - \chi_N)$ where χ_a is the susceptibility along the a-axis and χ_N is that perpendicular to the cleavage plane. From (2) we can directly get the angle which the χ_2 axis makes with the a-axis. This angle can also be calculated from the known values of $\chi_3 - \chi_N$ and $\chi_3 - \chi_a$, for,

$$\chi_3 - \chi_N = \chi_3 - (\chi_2 \sin^2\theta + \chi_1 \cos^2\theta)$$
$$\chi_3 - \chi_a = \chi_3 - (\chi_2 \cos^2\theta + \chi_1 \sin^2\theta).$$

Solving the simultaneous equation we get both θ and $\chi_3 - \chi_1$. In the case of the micas matters are very much simplified, since the χ_2 direction was found to coincide with the direction of the a-axis.

4. Experimental Precautions and Sampling of Specimens for the Anisotropy Measurements.

A careful selection of specimens for the magnetic determinations is absolutely essential, since inclusions and stains in mica are the rule rather

than the exception. Another serious difficulty in the case of rock minerals is that not only is the composition variable for varieties obtained from different localities but it might differ over different parts of the same specimen. The minerals are seldom perfectly homogeneous. For instance, inclusions may be very prominent in some regions of the same 'book' of mica, whereas other parts are clear and transparent. Often these inclusions consist of magnetite in dendrite-like forms. The presence of even small quantities of magnetite may be sufficient to cause considerable anomalies in the results. Other inclusions are, generally, flattened crystals of garnet, tourmaline and quartz in thin plates found between the sheets.

The micas were obtained in the form of small plates and of these the best were selected. These were further examined under a high power microscope and the portions containing included particles rejected. Satisfactory samples practically free from inclusions could be obtained. Inclusions in biotite are often associated with pleochroic haloes and afforded another test for their absence or presence. Phlogopite often shows asterism and this has been attributed to symmetrically arranged inclusions of rutile or tourmaline. Plates showing asterism were therefore rejected. In all cases, however, minute traces of inclusions mostly of submicroscopic dimensions were probably present.

The optical characteristics of the specimens were also examined under the polarising microscope. With convergent polarised light the muscovite specimens gave the usual biaxial interference figure, whereas the phlogopite and the biotite samples were sensibly uniaxial. No evidence of twinning was found in the plates taken up for examination. The optical axial plane is perpendicular to the *b* (010) plane in muscovite and parallel to the *b* (010) in phlogopite and biotite.

Only freshly cleaved plates were employed. These were further cleaned with dilute sulphuric acid, distilled water and alcohol.

In the case of mica, which was available in the form of thin plates only, we cannot neglect the effect due to the anisotropy of shape of the specimen. For the paramagnetic susceptibility is fairly high, especially in the case of the biotites, and in some cases the magnetic anisotropy also is comparatively small. The possible errors on this account were eliminated by adopting the devise of Krishnan of immersing the crystal in a liquid bath of the same mean susceptibility, for phlogopite and muscovite. An aqueous solution of manganese chloride was employed. For determining the anisotropy in the cleavage plane, which was found to be very feeble, discs of the material 5·5 mm. in diameter were prepared. In this case no correction for anisotropy of shape is necessary.

For the biotites the paramagnetic susceptibility was too high for a liquid-bath to be employed conveniently. Small plates 1 cm. by 4 mm. were cut out, cleaned with dilute acid and distilled water and placed one above the other to form a block $10 \times 4 \times 4$ mm. using traces of diamagnetic shellac for attaching them. Particular care was taken to see that the crystallographic directions of the plates coincided when cutting them out. The long edges were carefully rounded off so that a cylinder, 10 mm. height and 4 mm. diameter, was obtained. A silk thread was further wound round the cylinder so that the pieces might not fall off. It was finally cleaned with dilute sulphuric acid and distilled water. For determining the magnetic anisotropy in the cleavage plane discs 5·5 mm. in diameter were used. Only the value of $\chi_{\parallel r} - \chi_{\perp r}$ is given for biotite and phlogopite since the anisotropy in the cleavage plane was negligibly small.

The current through the electromagnet was adjusted by the use of a system of rheostats, and every time before the field was applied the iron was brought to a cyclic state by reversing the current several times. Uniformity of field over a large area was ensured by using flat pole-pieces of area 50 sq. cm. nearly.

The field strength was measured by means of a calibrated Grassot flux-meter and a standard search coil made by the author consisting of 30 turns of No. 40 s.w.g. double silk-covered copper wire wound round an accurately turned cylinder of non-magnetic marble, the diameter of the coil being 2·359 cm. Fields of the order of 1000–2000 oersteds were employed.

For mounting the crystal a thin glass fibre 1·5 cm. long and shaped like a pin was attached to the end of the quartz fibre with the pin-head down. The mica pieces were fixed to the pin-head by traces of pure shellac.

The torsional constant of the fibre was determined by suspending at its end a glass cylinder 0·327 cm. diameter and mass 0·0998 g. with its axis vertical and observing the period of oscillation, by the usual methods.

The mean of several independent determinations is given in Table I.

5. *Measurement of Absolute Susceptibilities.*

The mean susceptibility of the micas in the form of powder was determined by the Curie-Balance method. A torsion balance of the Curie-Wilson type was constructed by the author with a glass beam and glass extensions for supporting the phial holding the substance, all made of pyrex. A schematic diagram of the balance is shown in Fig. 1. The inhomogeneous magnetic field was obtained by keeping the pole pieces (specially designed by the author to go with an electromagnet made by Charles W. Cook & Son, Ashby de la Zouch) at an angle to each other. As is well known the

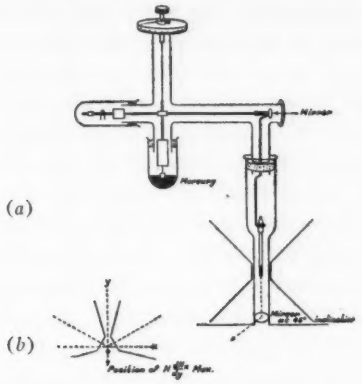

FIG. 1.

susceptibility is given by the formula

$$\chi = \frac{1}{m}\left\{\chi' m' + (\chi'' m'' - \chi' m')\left(\frac{F_{x_2} - F_{x_1}}{F_{x_3} - F_{x_1}}\right)\right\},$$

where χ, m represent the susceptibility and mass of the specimen, χ', m' of the air and χ'', m'' of the standard substance respectively, the masses referring to equal volumes of the substances.

F_{x_1} the force acting on the container alone measured by the torque on the torsion wire;

F_{x_2} the force acting on the phial + substance; and

F_{x_3} the force acting on the phial + standard substance.

All the usual precautions were taken, the most important being that the container is always brought back to the same position relative to the field when taking the measurements, and that the field is kept constant. The standard substances used was a solution of manganese chloride (33·8%) the susceptibility of which was accurately determined by the Quincke U-tube method.

6. Determination of Ferrous and Ferric Iron in the Specimens.

The percentage of total iron and ferrous iron in the micas were determined by the following methods.[12]

Total Iron.—The sample was ground to a fine powder in an agate mortar, and about 0·5 g. of the powder weighed in a platinum crucible and then fused with fusion mixture (two parts of Na_2CO_3 and one part of K_2CO_3). The fused mass after cooling was dissolved in dilute HCl in a silica dish, evaporated to dryness over a water-bath, redissolved in dilute HCl and the

silica filtered off, washed on the filter and weighed after ignition. The filtrate was heated up to boiling point and a little concentrated nitric acid added followed by 20 g. of ammonium chloride. Ammonia was then slowly added to the boiling solution until all the aluminium and iron were precipitated as hydroxide and the solution became slightly alkaline. The precipitate was then filtered off, washed on the filter with a warm solution of ammonium nitrate and ignited in a platinum crucible and weighed. The ignited mass was then fused with sodium bisulphate and after cooling dissolved in dilute sulphuric acid. The solution was then run through a Jones' reductor (an improved form of which has been devised by the author and reported elsewhere) in an atmosphere of carbon dioxide and finally titrated against standard permanganate.

Ferrous Iron.—The accurate determination of ferrous iron in silicate rocks is a matter of considerable difficulty. The modified Pratt method recommended by Hillebrand was adopted. A weighed quantity of mica was carefully ground in an agate mortar under pure alcohol for about an hour. A thorough grinding is necessary since coarse particles take a very long time to get dissolved in HF. The ground mass was carefully washed down into a platinum crucible with air-free water and 10 c.c. of cold dilute sulphuric acid added. The crucible was supported over a water-bath and surrounded by an atmosphere of CO_2 by the arrangement shown in Fig. 2. 6 c.c. of

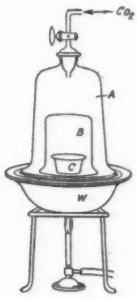

FIG. 2.

A.—Bell-jar; *B.*—Beaker; *C.*—Platinum crucible; *W.*—Water-bath.

40% hydrofluoric acid (Kahlbaum's analytical reagent) were quickly introduced into the crucible which was then covered with the lid and the water-bath heated, carbon dioxide being passed all the time. The reaction was allowed to go on for 3 hours. Meanwhile a solution containing 50 g. of boric acid and 20 c.c. of sulphuric acid in 300 c.c. of air-free water was prepared and the crucible and contents, after the reaction was over,

were quickly transferred into the cold boric acid solution and titrated immediately against standard permanganate, until a pink colour lasting for a minute or two was obtained.

A blank experiment was performed under similar conditions with ferrous ammonium sulphate. About 0·5 g. was weighed and dissolved in 300 c.c. of dilute sulphuric acid and immediately titrated against permanganate. Another 0·5 g. was weighed in a platinum crucible and the ferrous iron determined by the modified Pratt method as described above, using 6 c.c. of HF. The necessary correction was found to be + 0·28 c.c. of permanganate.

7. Measurement of the Pleochroism of the Micas.

A comparative measure of the pleochroism of the micas was obtained by the following experimental arrangement based on the principle of Cornu's method for determining the percentage of polarised light (Fig. 3).

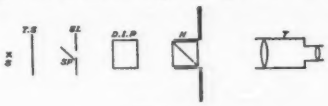

FIG. 3.

S.—Source of light; *T.S.*—Translucent Screen ; *Sp.*—Specimen; *Sl.*—Rectangular slit ; *D.I.P.*—Double-Image prism ; *N.*—Nicol mounted on circular scale ; *T.*—Telemicroscope.

The specimens were used in the form of thin plates, freshly cleaved, and of the same thickness 0·05 mm., selected from a very large number of cleaved plates. The mica plates were mounted behind the slit at an angle of 45° with the *b*-axes horizontal. The double-image prism was placed with the vibration directions vertical and horizontal, and the distance from the slit was adjusted until the two images, as seen through the telemicroscope, just touched one another. The horizontal vibrations are absorbed much more than the vertical and the images are of unequal intensity. By suitably rotating the nicol the intensities can be equalised. If 2θ is the angle between two positions of the nicol on either side of the vertical for which the intensities are equalised, then $\frac{I_V}{I_H} = \tan^2\theta$. A correction has to be introduced in the value of θ to eliminate errors due to reflection, etc., at the faces of the plates. For this a blank experiment was performed with a glass microscope coverslip of nearly the same refractive index as the mica plates and the necessary correction applied to the value of θ. The results are approximate only but afford a good comparative measure of the pleochroism of the micas.

The corrected values of $\tan^2\theta$ are given in Table III.

8. Results.

The results are presented in the tables shown below.

TABLE I. *Specific Magnetic Anisotropy of Phlogopite and Biotite. C.G.S. E.M. Units. Temperature* 25° C.

Specimen	Anisotropy $\chi_{\parallel}{}^{l} - \chi_{\perp}{}^{r}$ $\times 10^{6}$	Remarks
Phlogopite	1·38	The magnetic anisotropy in the cleavage plane was negligibly small in all cases and, therefore, only the values of $\chi_{\parallel}{}^{l} - \chi_{\perp}{}^{r}$ are given
Biotite (Canada) ..	6·25	
,, (Ural Mts.) ..	10·3	
,, (Bihar)	12·4	

Specific Magnetic Anisotropy of Muscovite.

Mode of Suspension	Orientation	Anisotropy $\Delta\chi \times 10^{6}$	Remarks
Cleavage plane horizontal	*b*-Axis perpendicular to the field	$\chi_2 - \chi_3 = 0{\cdot}11$	
b-Axis vertical	Cleavage plane parallel to the field	$\chi_2 - \chi_1 = 0{\cdot}70$	The χ_2 direction coincides with the *a*-axis
b-Axis horizontal and cleavage plane vertical	Do.	$\chi_3 - \chi_1 = 0{\cdot}61$	

TABLE II. *Mean Susceptibility of the Micas at* 25° C.

Specimen	$\bar{\chi} \times 10^{6}$
Muscovite	8·01
Phlogopite	7·85
Biotite (Canada)	30·8
,, (Ural Mts.) ..	40·6
,, (Bihar)	43·8

TABLE III.

Pleochroism of the Micas.

Specimens of thickness 0·05 mm.	$\text{Tan}^2\,\theta = \frac{I_V}{I_H}$
Muscovite	1·03
Phlogopite	1·09
Biotite (Canada) ..	1·58
,, (Ural Mts.) ..	1·89
,, (Bihar)	1·97

TABLE IV.

C.G.S. E.M. Units. Temperature 25° C.

Specimen, Description (Colour of the Biotites refers to very thin plates)	Mean Susceptibility $\chi \times 10^6$	Magnetic Anisotropy $\chi_{\parallel r} - \chi_{\perp r} \times 10^6$	$\chi_{\parallel r} \times 10^6$	$\chi_{\perp r} \times 10^6$	Total Iron %	Ferrous Iron %	Ferric Iron %	Magnetic Anisotropy referred to a ion of $Fe^{++} \times 10^6$
Muscovite .. Clear. Tinge of green	8·01	0·65	8·23	7·58	3·93	1·79	2·14	
Phlogopite .. Brownish yellow Submetallic lustre	7·85	1·38	8·31	6·93	4·34	3·18	1·06	2420
Biotite (Canada) .. Dark greenish brown	30·8	6·25	32·9	26·6	15·2	13·1	2·12	2670
Biotite (Ural Mts.) Dark brown	40·6	10·3	44·0	33·7	21·8	19·6	2·22	2930
Biotite (Bihar) .. Dark reddish brown	43·8	12·4	47·8	35·4	23·1	22·2	0·9	3120

9. Discussion of Results.

Both the susceptibility and the magnetic anisotropy are seen to depend upon the amount of iron present. The biotites exhibit a fairly large magnetic anisotropy and the paramagnetic susceptibility is also correspondingly high. The values for muscovite and phlogopite are comparatively small. In the case of the biotites the mean susceptibility is seen to increase with the percentage of iron almost linearly (Fig. 4).

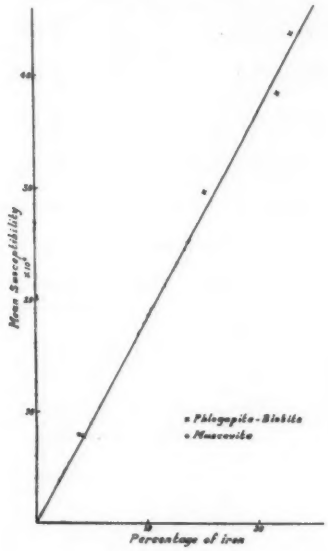

FIG. 4.

The total susceptibility of mica may be considered to consist of three parts, namely (1) that due to the ferrous iron, (2) that due to the ferric iron and (3) the contribution due to the other atoms. The first two are evidently paramagnetic terms while the last is diamagnetic. When the percentage of iron is large, as obtains in the case of the biotites, the diamagnetic term will be negligibly small as compared with the paramagnetic terms. But it will be considerable in muscovite and phlogopite which contain only about 4% of iron.

It will be of interest to calculate in a rough way the approximate Bohr magneton values for the biotites. The susceptibility of the biotites is amenable to theoretical considerations for the following reasons: (1) The percentage of iron is very high and we may neglect the diamagnetic term in the susceptibility; (2) Most of the

iron is present in the ferrous state ; (3) The disturbing effects due to possible minute traces of inclusions can be safely ignored. (In fact, the biotite samples were particularly free from defects.) Considering only the total iron present, the effective Bohr magneton value is obtained according to the formula $P_{B\ eff} = 2 \cdot 84 \sqrt{\chi_M T}$

	$P_{B\ eff}$
Biotite (Canada)	$= 5 \cdot 2$
,, (Ural Mts.)	$= 5 \cdot 0$
,, (Bihar)	$= 5 \cdot 0$

The values are seen to be much lower than the theoretical values to be expected in the case of the free paramagnetic ion just as in the case of other solid salts of iron. They are found to approach the spin only value of Fe^{++}, which is equal to $4 \cdot 92$ Bohr magnetons. The significance of this fact in the light of Van Vleck's theory of the quenching of the orbital moments by the crystalline electric fields in paramagnetic solids will be discussed later.

It is important to consider the effect of microscopic and submicroscopic inclusions on the magnetic anisotropy, especially in the case of muscovite which, according to the ideal formula $KAl_2\ (AlSi_3O_{10})\ (OH)_2$, cannot take in ferrous iron in the positions of six co-ordination replacing the aluminium atoms. We have to see if the magnetic anisotropy of muscovite is merely due to symmetrically arranged inclusions or if it can be of crystalline origin as in biotite, at least in part. If according to the ideal formula, the ferrous iron cannot form an integral part of the lattice, then apparently we are led to conclude that only the inclusions, microscopic or submicroscopic, are responsible for the anisotropy. But chemical analysis shows that very often the amount of ferrous iron present is much larger than can be accounted for by any of the common inclusions. For instance, in the muscovite sample examined by the author which contained inclusions of magnetite, the percentage of FeO is much larger than should be expected. The ferrous iron, therefore, is most probably present in the mica lattice itself in the positions of six co-ordination. The iron atoms should be present in groups to satisfy the rules of co-ordination and as such they really constitute a discontinuity in the lattice. We may regard them as being of the nature of inclusions of extremely small dimensions. This view gains support from the fact that biotite inclusions in muscovite are often met with and from what we know of the crystal structure of the micas a biotite inclusion can really be regarded as a discontinuity of the above character occurring over an extended region, magnesium also being present along with the iron in the positions of six co-ordination. Thus the anisotropy measurements throw an interesting sidelight and seem to provide evidence for the presence of discontinuities in the

lattice which cannot be detected by the microscope. The effect of inclusions on the magnetic anisotropy of the biotites will be comparatively negligible since, on one hand they are much less prominent and on the other the iron forming part of the lattice is present in very large amounts.

The close correspondence between the magnetic properties of the micas and their structure is very striking. In muscovite, as is to be expected from its pseudo-hexagonal structure, two of the principal susceptibilities lie in the cleavage plane and are nearly equal, while the susceptibility perpendicular to the plane is much less than either of the other two. In biotite and phlogopite two of the principal susceptibilities not only lie in the cleavage plane but are also of the same value. It must be emphasised, however, that the determination of the magnetic anisotropy in the cleavage plane was complicated by two factors namely, (1) strains and distortions set up when cutting out the specimens in the shape of discs and (2) the presence of microscopic inclusions. The spurious effects due to the first cause could be eliminated by exercising proper care in the preparation of the discs. The effect due to the second cause was studied by determining the magnetic anisotropy in the cleavage plane of a large number of spotted and stained samples of muscovite. The heavily spotted varieties always showed enormous anisotropy in the cleavage plane while those with perceptible traces of inclusions (magnetite) were anisotropic to the extent to which they contained the inclusions and this was considerable.

From the results it could be inferred that the contribution due to the minute traces of inclusion should be much less than the observed anisotropy in the cleavage plane, and that at least part of the observed anisotropy in the cleavage plane is genuine. The definite orientation of the *b*-axis in the magnetic field in all cases also leads to the same conclusion. In this connection the isotropy of phlogopite and the biotites in the cleavage plane is interesting. It proves that the disturbing effects due to any inclusions present are negligible. Samples of phlogopite which exhibited marked asterism showed considerable anisotropy in the cleavage plane. There is a close similarity between the optical and magnetic properties also, when we remember that the muscovite showed a biaxial interference figure whereas the phlogopite and the biotites were sensibly uniaxial.

Magnetic Anisotropy and Chemical Constitution.—The specific magnetic anisotropy is plotted as a function of the total iron, ferrous iron and ferric iron respectively in Fig. 5. Since phlogopite and biotite belong to the same group we can study the characteristics of this group from the results obtained. In the first place there seems to be no obvious connection between

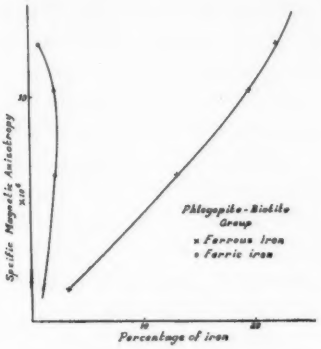

FIG. 5.

the ferric iron content and the anisotropy. On the other hand, the magnetic anisotropy increases smoothly with the percentage of ferrous iron. But the relationship is not linear and for large percentages of fron the curve becomes steeper. In Table IV the gram ionic anisotropy for Fe^{++} is given. This shows a remarkable increase with the percentage of ferrous iron in the biotites (Fig. 6). It is likely that this increase is due to interaction between

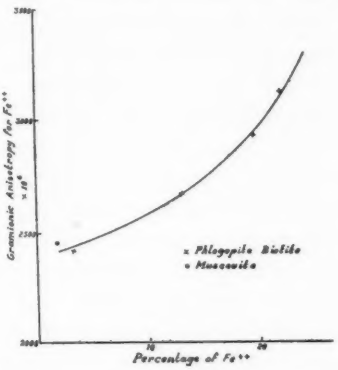

FIG. 6.

neighbouring iron atoms in the sheet. The nature of this interaction will be discussed later.

The results obtained are significant in the light of recent theoretical developments due to Van Vleck and Penney and Schlapp.

Van Vleck's Theory of the Paramagnetism of Solids.—The object of the theory is to account for the following features in the magnetic behaviour of paramagnetic solids, such as (1) the departure from the Curie law and the

appearance of cryomagnetic anomalies at low temperatures, (2) the relative contributions of the spin and orbital moments to the susceptibility and (3) the magnetic anisotropy of the crystals. It is based on the earlier work of Bethe and Kramers on the Stark splitting of the energy levels of atoms and ions under the influence of crystalline electric fields. Detailed computations have been made by Penney and Schlapp, who have considered Pr and Nd among the rare earths and Co, Cr and Ni in the iron group. Jordahl has made calculations in the case of the cupric salts. The main results for the salts of the iron group are as follows: Since the magnetically effective 3d electrons are in the outermost shell, the influence of the crystalline electric fields due to the neighbouring atoms will be strong enough to break the coupling between the orbital and spin moments. The orbital degeneracy is partially or completely removed and the orbital moment makes practically no contribution to the susceptibility. The orbital moment is then said to be quenched. The spins, however, are not directly affected by the crystalline fields and hence contribute fully to the susceptibility. An asymmetric crystalline field produces asymmetric partial freezing of the orbital moment and due to the coupling between orbit and spin, since the remnants of the orbital moment are anisotropic, the freedom of the spins to orient themselves along different directions will be different. Hence the crystal exhibits magnetic anisotropy. Due to the partial quenching of the orbital moments the susceptibility lies between the limits given by $P_{B'} = \sqrt{4S\,(S+1)}$ and $P_{B'} = \sqrt{4S\,(S+1) + L\,(L+1)}$. In fact we have pointed out earlier that in the case of the biotites this is the case, the Bohr magneton values approaching the spin only value. One important consequence of Van Vleck's theory is that manganous and ferric salts should not exhibit any marked anisotropy, since the Mn^{++} and Fe^{+++} ions are in the S-state and therefore have no orbital moment to be quenched. The present investigation also shows how the magnetic anisotropy of biotite is not dependent on the amount of ferric iron in the specimens, and thus lends support to the theory.

In many hydrated paramagnetic crystals which exhibit large magnetic anisotropy, there is evidence from X-ray analysis that we have an octahedral arrangement of water molecules round the paramagnetic ion. Recent experimental work shows that the crystalline electric field due to such an arrangement deviates widely from cubic symmetry[13] and most probably possesses only hexagonal symmetry. Usually in such paramagnetic crystals there are a number of these complexes (formed by the paramagnetic ion and its environment of six water molecules) in the unit cell, differently oriented with respect to each other, such that crystalline magnetic properties may have only the lower rhombic symmetry. But in the micas the case is much

simpler. Here the octahedral group around the Fe^{++} ion consists of four oxygen atoms and two hydroxyl groups and all the groups are arranged parallel to each other in layers in the crystal lattice. Hence the anisotropy of the crystal actually corresponds to that of these individual paramagnetic complexes. The hexagonal symmetry of phlogopite and biotite as regards the magnetic properties lends support to the view that the crystalline electric fields due to the octahedral grouping possess the same symmetry. In the case of muscovite, however, the departure from hexagonal symmetry may be attributed to the staggering of the sheets relative to each other which is responsible for the monoclinic angle of 95° and which probably introduces slight departures from the octahedral symmetry of the environment round the Fe^{++} ion. Since the 3d electrons occupy the outer shell they are very susceptible to slight changes in the positions of the surrounding atoms which can cause considerable variation in the character of the crystalline fields influencing these outer electrons. The magnetic anisotropy of the paramagnetic complex $[(Fe(OH)_6]$ referred to a gram ion is most probably the value obtained for phlogopite since, here, the magnetic dilution is large enough for the interaction due to neighbouring paramagnetic atoms to be ignored.

The rapid increase in the magnetic anisotropy of the biotites with the percentage of iron is a new feature and gives an insight into the effect of the concentration of the paramagnetic ion on the magnetic anisotropy. The explanation in this case seems to be that it is due to the interaction between neighbouring iron atoms. The peculiar structure of mica is very favourable for such interaction to take place since the iron atoms lie all in the same plane and their population is sufficiently high in the biotites for most of them to occupy neighbouring positions of six co-ordination. Interactions of this character are not taken into account by Van Vleck's theory which is strictly applicable only in the case of salts of considerable magnetic dilution, *e.g.*, the highly hydrated sulphates and double sulphates of the transition elements.

These interactions are the 'exchange effects' or 'Austausch' discovered by Heisenberg. The exchange effects are formally equivalent to a strong coupling between the spins of the interacting electrons and take place when the interatomic distance has a critical value in ferromagnetics (2·7–3 Å according to Forrer, in the case of iron). In the biotites, however, the distance between positions of six co-ordination is of the order of 2·6 Å which is less than this critical value. For explaining the experimental results it is enough to assume that the effect of these interactions is equivalent to imposing a further restriction on the freedom of orientation of the orbital moments. This will naturally increase the magnetic anisotropy. At the

same time we should expect a decrease in the Bohr magneton value due to the further quenching of the orbital moments. This is actually found to be the case, for we find that with the increase in the percentage of iron there is a corresponding decrease in the approximate effective Bohr magneton value. Thus the explanation offered seems to be quite satisfactory although the exact nature of the interaction has to be investigated further.

10. Pleochroism of the Biotites.

There is, as yet, no satisfactory explanation of the pleochroism of the biotites. The intimate relationship between colours of inorganic salts and paramagnetism is well known, for salts of the transition elements which are coloured are also paramagnetic. Saha[14] has put forward a theory of the origin of colour in inorganic salts according to which absorption in the visible region of light is due to transitions involving the reversal of the spin vector of the one of the 3d electrons of the paramagnetic ion. Such transitions although forbidden for the free paramagnetic ion are assumed to be possible in solids and in solutions. Subsequent work by Bose and others lends support to this view.

The connection between colour and paramagnetism at once suggests a corresponding relationship between pleochroism and paramagnetic anisotropy and the examination by the author of the available data on the pleochroism and paramagnetic anisotropy of salts of the iron group of elements has revealed that strong paramagnetic anisotropy is generally associated with marked pleochroism. This enquiry proved to be fruitful in another way. The author could not find any reference to the pleochroic properties of $FeSO_4$, $(NH_4)_2\,SO_4$, $6H_2O$ in the literature on the subject. This substance is known to be highly anisotropic magnetically and we should expect a marked pleochroism also. A large single crystal was examined in the (010) plane and it was found that the colour is pale green for light vibrations in the γ direction and yellow when the vibrations are in the α direction.

The bearing of the above on the pleochroism of the biotites is obvious, for we have seen that pleochroism is most pronounced in the varieties rich in ferrous iron and the magnetic anisotropy also increases with the iron content. The two phenomena are evidently closely related. If the mechanism of absorption of light in biotite by the iron atom is the same as suggested by Saha (The positions of the absorption maxima are slightly different in the different specimens and seem to correspond roughly with the $^6D - {}^4P$ and $^6D - {}^4F$ = transitions for Fe^{++}) the pleochroism implies that the reversal of the spin vector can take place only when the light vibrations are parallel to the cleavage plane and not when they are perpendicular. This

restriction in the orientation of the spins is evidently due to the influence of the asymmetric crystalline fields which, according to Van Vleck, act indirectly on the spins through the spin orbit coupling and which are responsible for the large magnetic anisotropy.

The close correspondence between the ease of magnetisation parallel to the cleavage plane (the paramagnetic susceptibility parallel to the cleavage plane is much greater than that perpendicular to it) and the readiness with which the spins respond to the electric field of light wave when this is parallel to the cleavage plane is very striking and is strongly suggestive of the fact that the polarisation of absorption in the biotites is chiefly due to the influence of the assymmetric crystalline fields acting on the paramagnetic ion enhanced, however, by the spin–spin interactions. The recent work of Krishnan and Chakrabarty[15] on the polarisation of the absorption lines of single crystals of the hydrated sulphates of Pr and Nd is interesting in this connection. They find that " many of the absorption lines are strongly polarised, some of them being confined almost wholly to vibrations along one or another of the principal axes of the optical ellipsoid of the crystal and that these variations in the direction of polarisation occur even among the lines of the same group, in other words, among the Stark components which originate from the same absorption line of the free ion, some are polarised strongly in one direction and some strongly in another." These crystals also show strong magnetic anisotropy. From these facts Krishnan concludes that the crystalline electric fields which produce the Stark splitting are also highly anisotropic.

The nature and disposition of the magnetic carriers in biotite may now be understood from the following picture. The orbital moments being mostly frozen, the freedom of orientation of the spins is also restricted considerably. We assume that the spins are mostly oriented with the magnetic axes nearly parallel to the cleavage plane, randomness of orientation existing in azimuth, so that there is no residual magnetisation as should be the case in paramagnetics. The magnetic carriers possess complete freedom of orientation in the cleavage plane. Under the influence of a magnetic field parallel to the cleavage plane, we get the usual paramagnetism although considerably diminished in magnitude. But when the field is normal to the cleavage plane, the resolved part of the spin moments perpendicular to the cleavage plane is much less on account of the restrictive action of the crystal fields, and we get a much lower susceptibility. Thus the high magnetic anisotropy may be explained. Our picture also reveals how the reversal of the spin vector can take place in the cleavage plane but not perpendicular to it since the spins are directed more or less parallel to

the cleavage plane. The pleochroism also is thus satisfactorily explained. This physical picture although somewhat naive is sufficient to explain both phenomena in a crude way. A rigorous treatment of pleochroism taking into account the Stark splitting of the energy levels in the crystal fields is very desirable.

It seems very likely that the mutual interaction of neighbouring paramagnetic ions, to which we ascribed the enhanced anisotropy in the varieties rich in iron, plays a significant part in intensifying the pleochroism, although at present we cannot say to what extent. But it is seen that when the percentage of ferrous iron exceeds a certain value, the effect due to the interaction of the iron atoms may become enormous as compared with the usual Van Vleck effect of the asymmetric fields, and both the magnetic anisotropy and the pleochroism become exceedingly large.

Although the connection between pleochroism and paramagnetic anisotropy seems to be obvious in the biotites, further quantitative investigation is necessary in the case of other paramagnetic salts to establish the generality of the relationship. Some anomalous features also have to be explained. For instance, Murmann and Rotter have observed pleochroism in $MnSO_4$, $(NH_4)_2\ SO_4$, $6H_2O$[16] although this crystal is almost isotropic magnetically. Again in the case of a rose-coloured variety of tourmaline containing a considerable percentage of manganese the author has observed pronounced pleochroism, the absorption band in green being very strongly polarised, while the magnetic anisotropy is very feeble. The crystal is paramagnetic. $\chi = 0{\cdot}31 \times 10^{-6}$, $\chi_\perp{}^r - \chi_{||}{}^l = 0{\cdot}008 \times 10^{-6}$ *c.g.s.* E. M. units. This would indicate that at least as regards relative magnitudes, in all cases, pleochroism and magnetic anisotropy bear no simple relationship to each other.

A quantitative study of the polarisation of the absorption bands of paramagnetic crystals of salts of the iron group of elements, in relation to their magnetic anisotropy is under progress in order to further elucidate the connection between the two phenomena.

My heartfelt thanks are due to Sir C. V. Raman, F.R.S., N.L., for suggesting the problem and for his encouragement and helpful criticism. I also wish to express my indebtedness to Mr. N. Jayaraman for his assistance while doing the chemical analysis and to Dr. K. R. Krishnaswami, D.Sc., for kindly providing me with facilities for the same.

Summary.

The paramagnetic anisotropy and susceptibility of three different varieties of biotite and one each of muscovite and phlogopite have been

determined. The ferrous and ferric iron contents of the specimens have also been found by chemical analysis and their pleochroism estimated quantitatively. It is found that the biotites are highly anisotropic and that both the anisotropy and the pleochroism increase with the iron content. The magnetic anisotropy is seen to depend only on the amount of ferrous iron and not on the ferric iron. The relationship between the gram ionic anisotropy referred to Fe^{++}, and the percentage of iron is not linear when the latter is high. The anisotropy, in fact, increases more rapidly and this is attributed to the mutual interactions of neighbouring paramagnetic atoms, which cannot be neglected for high concentrations of the latter. The results, in general, are in agreement with the theory of the paramagnetism of solids recently developed by Van Vleck and Penney and Schlapp based on the Stark splitting of the energy levels of the paramagnetic ion under the influence of the strong asymmetric crystalline electric fields. The pleochroism of biotite is discussed in the light of Saha's view that absorption of light in inorganic salts of elements of the transition series is due to transitions involving the reversal of the spin vector of one of the 3d electrons of the cation. In biotite where the absorption is essentially due to the ferrous iron, the pleochroism is explained as being due to the fact that the reversal of the spin vector of the 3d electrons of the Fe^{++} ion can take place only when the light vibrations are parallel to the cleavage plane. This restriction on the spins is attributed to the influence of the asymmetric crystalline fields which according to Van Vleck's theory give rise to the magnetic anisotropy also. This affords a satisfactory theoretical explanation of the origin of pleochroism besides indicating the character of its intimate relationship with paramagnetic anisotropy, observed experimentally.

REFERENCES.

1. E. Wilson .. .. *Proc. Roy. Soc.*, 1920, **96**A, 429.
   G. Grenet .. .. *Ann. de Physique*, 1930, **13**, 263.
2. E. Wilson .. .. *Loc. cit.*
3. W. L. Bragg .. .. *The Atomic Structure of Minerals*, Humphrey Milford, Oxford University Press, 1937.
4. W. G. Penney and R. Schlapp *Reports on Progress in Physics*, 1935, **2**, 60.
5. L. Pauling .. .. *Proc. Nat. Acad. Sci.*, 1930, **16**, 123.
6. W. W. Jackson and J. West.. *Zeit. F. Krist.*, 1930, **76**, 211; 1933, **85**, 160.
7. Kunitz .. .. *Neus. Jb. Min. Geol. Paläut.*, 1924, **50**, 365.
8. Niggli .. .. *Zeit. F. Krist.*, 1937, **96**, 89.
9. G. Nagelschmidt .. .. *Ibid.*, 1937, **97**, 514.
10. C. Mauguin .. .. *C. R.*, 1927, **185**, 288; 1928, **186**, 879 and 1131.
11. K. S. Krishnan, *et al.* .. Papers in the *Phil. Trans. Roy. Soc.*, (A), 1933–37.

12. Hillebrandt .. .. *The Analysis of Silicate and Carbonate Rocks*, Washington, 1916.
13. K. S. Krishnan and A. Mookerjee .. .. *Nature*, 1937, **140**, 549.
14. M. N. Saha .. .. *Nature*, 1930, **125**, 163.
15. Krishnan and Chakrabarty .. *Jour. Chem. Phys.*, 1938, **6**, 224.
16. Murmann and Rotter .. *Sitz. Berich. Akad. Wien.*, 1858, **27**, 172; 1859, **34**, 158.

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